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Contributor contact details

(* = main contact)

Editor

M. Clark
Department of Colour Science
University of Leeds
LS2 9JT
UK

E-mail: m.clark@leeds.ac.uk

Chapter 1

D. M. Lewis
Department of Colour Science
University of Leeds
LS2 9JT
UK

E-mail: d.m.lewis@leeds.ac.uk;
davebarblewis@hotmail.co.uk

Chapter 2

A. K. Roy Choudhury
Government College of
Engineering and Textile
Technology
Serampore
Hooghly 712 201
West Bengal
India

E-mail: akrc2008@yahoo.in

Chapter 3

J. Koh
Department of Textile Engineering
Konkuk University
1 Hwayang-dong, Kwangjin-gu
Seoul 143–701
South Korea

E-mail: ccdjko@konkuk.ac.kr

Chapter 4

N. A. Ibrahim
Textile Research Division
National Research Centre
El-Behouth St
PO Box 12622
Giza

Egypt

E-mail: nabibrahim49@yahoo.co.uk;
nabibrahim@hotmail.com

Chapter 5

R. J. W. Hefford
Independent Cosmetic Advice Ltd.
56 Linden Way
Ponteland
Newcastle-Upon-Tyne
NE20 9JF
UK

E-mail: rjwhefford@btinternet.com

Chapter 6

M. Wainwright
School of Pharmacy and
Biomedical Science
Liverpool John Moores University
Liverpool
L3 3AF
UK
E-mail: mark_wainwright@hotmail.
com

Chapter 7

B. Kaur and S. N. Bhattacharya*
Rheology and Material Processing
Centre
RMIT University
Melbourne
Victoria 3000
Australia
E-mail: Satinath.Bhattacharya@
rmit.edu.au

Chapter 8

A. P. Damant
Scientific Methods and Laboratory
Policy Branch
Food Standards Agency
Aviation House
125 Kingsway
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WC2B 6NH
UK
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D. M. LEWIS, The University of Leeds, UK

Abstract: Perceived and real environmental threats have greatly influenced wool dyeing trends and much of these effects are detailed. In particular chrome dyeing has been under scrutiny and methods to avoid the use of extremely toxic Cr(VI) compounds are discussed. Damage in wool dyeing is an important theme and the use of anti-setting agents in wool dyebaths is fully described along with their *modus operandi*. In the latter case reactive dyes have much to offer especially in the case of those reacting by a Michael addition mechanism. Shrink-resist treatments to give machine-washable wool are discussed in terms of required dye selection and also the environmental hazards of Absorbable Organo Halogen (AOX) production if pre-chlorination is used. Recent developments in ink-jet printing and how they should favour wool fabric printing are described.

Key words: wool chemistry, acid dyes, chrome dyes, reactive dyes, dyeing theory, dyeing machine-washable wool, damage and wool setting, ink-jet printing.

1.1 Introduction

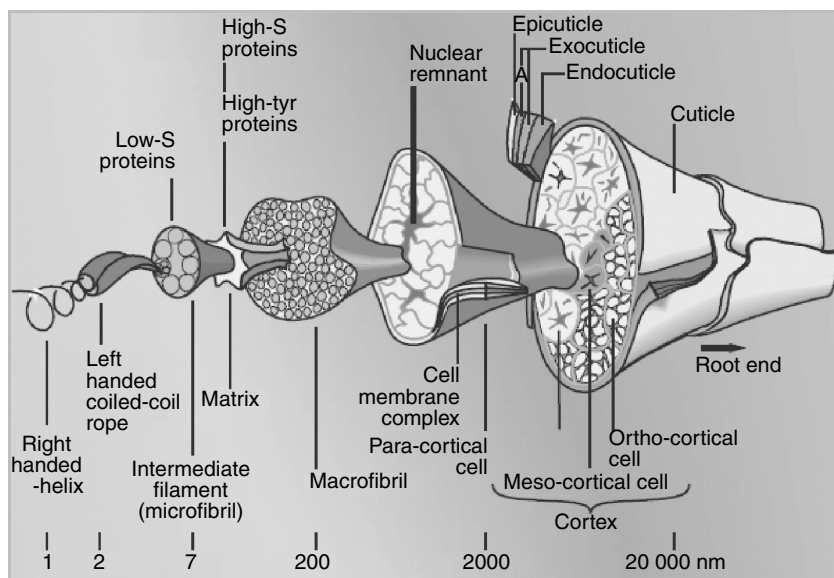
Animal fibres such as wool, cashmere and alpaca are highly prized when made into garments since these exhibit desirable properties such as soft touch, warmth, beautiful drape, excellent comfort in wear and, using modern synthetic dyes, unparalleled colouration possibilities with very few shade restrictions. Leeder¹ points out that wool has been bio-engineered over millions of years to be worn next to an animal's skin, and is thus better than other types of fibres in terms of comfort in wear; it possesses the properties of absorbing up to 30% of its own weight of water without feeling wet, and even giving out heat when it absorbs water. Despite the above strong positives it has to be noted that wool makes up less than 5% of the textile market, cotton and synthetic fibres making up the bulk – it would not be possible for wool growing to increase significantly and therefore wool must position itself mainly in the desirable 'luxury' item sector of the market. There are also performance disadvantages, which are not present in garments made from the other textile fibres; these include felting shrinkage (in knitwear this can be as high as 60%) during household laundering

procedures, the need to scour the raw wool to remove lanolin, soil and seeds, and attack by moths and beetles during garment storage.

Wool scientists are well aware of the beautiful composite structure of the wool fibre; a single fibre is made up of many thousands of different proteins and even some 15% of non-protein material; nature has designed, through evolution, each of these components to play a role in protecting the animal from the elements and in maximising the animal's comfort. The widely acclaimed, classic diagram showing the amazing complexity of the fibre, produced by Fraser and co-workers at Commonwealth Industrial Scientific Organisation (CSIRO)'s Division of Protein Chemistry in Melbourne, is shown in Fig. 1.1.

Not shown in this diagram is the F-layer which coats the epicuticle with a hydrophobic barrier; the classic studies by CSIRO scientists and others have established that this layer is made up of fatty acids covalently bonded to the fibre through thiol ester bonds at the cysteine site. The major constituent of this lipid material is 18-methyleicosanoic acid. The proteins in the epicuticle are highly disulphide cross-linked (i.e. cystine rich); in fact in the A-layer one in every 2.5 residues is cystine, making these surface proteins as hard as hoof material. These observations are crucial in understanding dye-diffusion processes when dyeing wool from aqueous solution as the surface structure creates a barrier to dye diffusion.

The marketplace is increasingly sensitive to possible negative impact of processing products on the environment; this has implications across the



1.1 The microscopic structure of a wool fibre.

whole range of manufacturing processes used. This statement actually has profound implications for the finisher, dyer and printer of wool materials. In this context heavy metals present in dyes or in dyeing processes are important issues; although reactive dyes are being used more and more as replacements to produce dyed materials having high wet-fastness properties they do not give the same level of light-fastness in pale depths as do dyeings produced with pre-metallised or after-chrome dyes.

Compared to cotton and synthetic fibres, wool lacks brilliance in white and pastel shades and this has been seen as a major market issue; resolution of this problem will come from further research into improving the photostability of the base wool fibre^{2,3} and developing novel bright chromophores, even those not normally suited for dyeing wool.

To prevent felting shrinkage processes based on chlorination pre-treatments are often used but these give relatively high amounts of Absorbable Organo Halogen (AOX) residues – the colourist has to be aware that up to 1000 mg/L AOX can be discharged from dye-houses dyeing these pre-treated substrates; it is vital that such pre-treatments are replaced by non-chlorine surface oxidation processes without adversely affecting dyeing properties.

Wool and other animal fibres undergo ‘setting’ reactions during dyeing, the extent of these depending on bath pH, time and temperature; the amount of set imparted influences final fibre strength and other properties such as yarn bulk. The interesting sulphur chemistry behind these reactions will be reviewed, emphasising the value of using so-called anti-setting agents in the dyeing process to improve final wool quality.

Ink-jet printing textile fabrics is now well established; in particular this procedure is ideally suited to wool printing; wool printing was a very small-scale activity in the past since screen printing required considerable investment in preparing and storing screens which could not be justified in terms of the short run-lengths involved. The special factors limiting the rapid adoption of such digital technologies for wool fabric printing will be considered.

1.2 Overview of industry practice

Prior to dyeing wool has to be scoured in the so-called raw state to remove dirt, soil, some vegetable matter, suint and lanolin or wool grease; scouring is usually carried out with non-ionic detergent and optionally sodium carbonate at 40–50°C. This cleaned loose wool is then combed or carded to remove residual vegetable matter; combing is done on longer fibres to produce tops which are then spun on the worsted yarn system; the woollen system tends to use carded, shorter, coarser fibres. Wool may be dyed in the raw, loose fibre form, top form, or in yarn form or in piece form; dyeing is

typically carried out at the boil for usually 1 h, although with current high energy costs there is increasing interest in reducing dyeing temperatures.

In the current high fashion industry it is more desirable to leave colouration to the later stages and even, in the case of knitwear, to dye in the garment form. The stage at which wool is dyed critically affects dye selection; machinery with low fibre–liquor interchange demands the use of dyes with excellent levelling or migration properties, particularly in the case of hank dyeing of yarn or in piece dyeing on the winch – these dyes unfortunately give rise to poor wet-fastness properties in the final article. The converse to the above point is that dyes with lower migratory ability should be applied in machines giving excellent fibre–liquor interchange and such dyeings can exhibit excellent wet-fastness properties in the final article; machinery selection to allow effective use of these dyes includes package machinery for yarn dyeing and soft-flow jet machines for piece dyeing.

Unlike cotton and cotton blends there is very little interest in continuous or semi-continuous dyeing of wool even though it has been demonstrated that pad-batch dyeing of wool in piece or top form is perfectly feasible at room temperature; the reason for this lack of interest lies in the short runs usually available to dye a particular shade in the wool industry.

1.3 The theoretical basis of wool dyeing

1.3.1 Anionic or so-called acid dyes in wool dyeing

Wool is a heterogeneous mixture of proteins; it may be coloured with a variety of water-soluble dyes but in practice it is invariably dyed and printed with sulphonated dyes. Wool has been, and still is to some extent, dyed with simple, low molecular weight (*circa* 400–800 Da), sulphonated chromophores, termed ‘acid dyes’; as the dye manufacturing and the dye-using industries grew more sophisticated these acid dyes were modified, usually by increasing their molecular size, to give better washing and light-fastness properties. Thus acid-milling dyes, chrome dyes, pre-metallised dyes and reactive dyes all find use in various application sectors. The simplest way to write an acid dye structure is as $D(-SO_3^-Na^+)_n$ where D is a chromophoric entity which may be substituted azo, anthraquinone, phthalocyanine or others, and n is an integer, usually 1–3.

Since it is made up of many different amphoteric protein macro-molecules, according to the pH and temperature of the surrounding solution, the constituent proteins in wool can show clear differences in charge; these differences are brought about by protonation or deprotonation of carboxylic and amino side-chain functionalities. Assuming basic side chains are derived

from lysine ϵ -amino, histidine imidazolyl and arginine guanidinium residues the following describes this situation:

pH 2–4

LysNH₃⁺...3.1 Mol % [269 μ mol/g] Glu-COOH.....11.9 Mol % [1049 μ mol/g]
 His-Im⁺....0.9 Mol % [82 μ mol/g] Asp-COOH.....6.4 Mol % [560 μ mol/g]
 Arg-Guan⁺...6.8 Mol % [600 μ mol/g]
 Total amino acids giving positive charge10.8 Mol %
 Total amino acids giving negative charge0.0 Mol %
Thus the fibre carries an overall positive charge.

pH 4–12

LysNH₂/ NH₃⁺.....3.1 Mol % Glu-COO⁻.....11.9 Mol %
 His-Im.....0.9 Mol % Asp-COO⁻.....6.4 Mol %
 Arg-Guan⁺.....6.8 Mol %
The overall charge on the fibre is neutral to negative

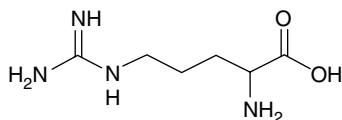
pH 12+

LysNH₂.....3.1 Mol % Glu-COO⁻.....11.9 Mol %
 His-Im.....0.9 Mol % Asp-COO⁻.....6.4 Mol %
 Arg-Guan.....6.8 Mol %
Overall fibre charge is negative as practically all amino functions are deprotonated.

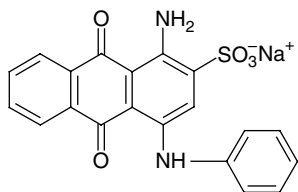
The above analyses are approximations and are governed by the acid dissociation constants of the $-\text{NH}_3^+$ and $-\text{COOH}$ residues, conveniently expressed as pK_a values; for example at 25°C lysine ϵ -amino has a pK_a value of about 10.5 and the glutamic acid terminal carboxylate is about 4.2. Possibly of even greater significance, in terms of positive charge contribution, is the guanidyl side-chain arising from the amino acid arginine, present at 6.8 Mol % in wool, as against lysine 3.1 Mol %.⁴ Arginine has the structure as shown in Fig. 1.2.

The pK_a value of the protonated guanidinium group is 12.5 and its abundance in wool makes this a most important site for ionic interactions with anionic sulphonated dyes.

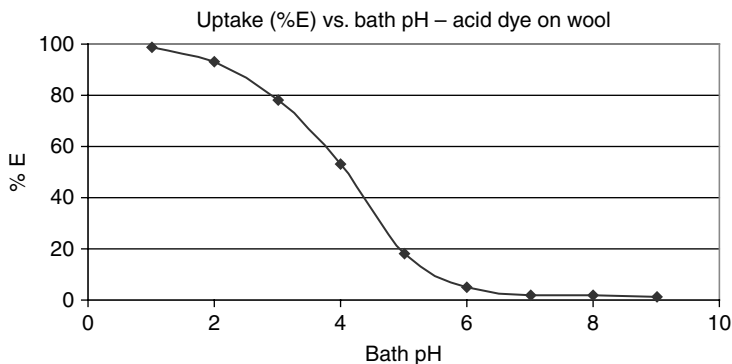
Acid levelling dyes are usually monosulphonated and dye wool from boiling dyebaths under acidic conditions (pH 3–4). The acid dye structure is typical as shown in Fig. 1.3.



1.2 Arginine.



1.3 C. I. Acid Blue 25.



1.4 Acid dye absorption versus bath pH.

The small molecular size of acid dyes means that there is very significant dye migration during their boil application, allowing good coverage of tippy wools and also for their application in dyeing systems where there is limited interchange between liquor and goods, e.g. piece dyeing in winches and hank dyeing of yarns. This ready migration is a disadvantage in washing processes giving rise to colour wash-down and staining of certain white adjacent fabrics in the laundry load.

Wool is usually dyed at the boil for 1 h with acid dyes; if bath 'exhaustion' (exhaustion or %E is a commonly used dyer's term for the amount of dye absorbed by the fibre) is measured at the end of dyeing and plotted against bath pH, then the typical curve shown in Fig. 1.4 is obtained.

Acid-milling dyes are of greater molecular size than the above simple dyes and exhibit high 'neutral' (pH 5–7) substantivity for the wool fibre (i.e. the curve in Fig. 1.4 is shifted to the right – even E values of about 80% at pH 7.0 can be obtained); the dyeings produced with these dyes have good fastness to water and mild washing treatments coupled with good light-fastness. A typical example of this type of milling dye structure is shown in Fig. 1.6.

Acid-milling dyes, due to their lower migration properties, find use in dyeing machines where there is good liquor–fibre interchange and these include package dyeing of wool yarn and soft-flow jet dyeing of wool piece goods.

Pre-metallised dyes fall into two categories; the older 1:1 dye:metal complex and the later 2:1 dye:metal complexes. The complexing metal cations are either chromium⁽³⁺⁾ or cobalt⁽³⁺⁾. The application conditions for these two classes of dye are quite different – the former are dyed at pH 1–2 to achieve maximum levelling, as required for piece dyeing, whereas the latter are dyed at pH 6–7 since they have very high substantivity due to their large molecular size and hydrophobicity. Comprehensive reviews^{5, 6} covering the synthesis and the application of pre-metallised dyes to wool are available.

1.3.2 Physical chemistry of wool dyeing

Classical wool dyeing theories such as Gilbert–Rideal or the Donnan membrane theory attempt to model the physical chemistry of wool dyeing according to electrostatic principles.^{7,8} It is the author's opinion that the assumptions made when applying the above approaches to the wool dyeing system cannot take into account the bewildering complexity and heterogeneity of the wool fibre proteins – considering wool is made up of thousands of different proteins a reasonable question might be posed: 'which protein is being dyed?' Any answer to this question must take note of the fact that the major protein components being dyed will depend on bath pH, bath temperature and dyeing time. An additional complication is that fibre structure changes physically and chemically during the boiling process.

The following is therefore an attempt to explain some of the more puzzling aspects of acid dye absorption by wool. As mentioned above, the initial driving force for dyeing to occur with a simple acid dye/polyamide fibre combination is undoubtedly Coulombic, but, depending on dye structure, non-polar interactions are also capable of playing an important role. In terms of Coulombic interactions, an important factor which affects the rate of acid dye uptake and its final saturation value on the fibre is the total number of protonated amino sites in the fibre. In this context it is valuable to make a comparison between wool, silk and nylon (Table 1.1).

Thus one may expect the saturation values of acid dyes on these three polyamide fibres to be in the same ratio as the above basic group contents, i.e. wool:silk:nylon = 23:4:1. This effect was verified experimentally by Skinner and Vickerstaff⁹ who studied the equilibrium uptake of C.I. Acid Blue 45 (1,6-diamino-4,8-dihydroxy-3,7-disulpho-anthraquinone) on the above three polyamide fibres at pH 1.6 and 85°C; the corresponding ratio obtained was 14:4:1.

The effect of varying the number of sulphonate groups in the dye molecules on the substantivity of acid dyes for nylon, wool and human hair, has been examined by numerous studies.^{7–13} These researchers clearly

Table 1.1 Amino groups in wool, silk and nylon

Wool	Lysine primary amino plus histidine secondary/tertiary amino plus arginine guanidino plus α -terminal amino	820 $\mu\text{mol/g}$
Silk	Lysine, plus histidine plus α -terminal amino	150 $\mu\text{mol/g}$
Nylon 6,6	α -Terminal amino	36 $\mu\text{mol/g}$

demonstrated that dye substantivity for the polyamide substrates decreases in the following order:

monosulphonate > disulphonate > trisulphonate > tetrasulphonate.

The above observations mean it is important to consider the various types of molecular interactions which may occur in dye–fibre systems. In terms of non-covalent interactions, the different interactive forces between two molecules, like or unlike, can be divided into five categories:¹⁴ Van der Waals (VDW) forces, electrostatic interactions, induction forces, charge transfer stabilisation effects and solvophobic interactions.

In terms of dyeing processes the forces which have sufficient size to be of importance are:

- (i) *VDW interactions*; these non-covalent molecular interactions are the sum of dispersion and repulsive energies. The thermodynamic strength of VDW interactions¹⁵ is smaller than 8 KJ mol⁻¹.
- (ii) *Electrostatic interactions between static molecular charge distributions*; in dyeing processes these include not only, for example, obvious attractions such as those between protonated amino groups in polyamide fibres and sulphonated anionic dyes, but also, according to classical definitions, hydrogen bonding.¹⁴ A recent review points out that this may be an inadequate definition¹⁶ but for the purposes of this analysis it is suitable. Hydrogen bond strengths vary considerably; in the case of the hydrogen bond between neutral molecules they are in the range 10–65 KJ mol⁻¹ and when one of the components is ionic this range rises to 40–190 KJ mol⁻¹.
- (iii) *Solvophobic or hydrophobic interactions*; these arise from the effect of non-polar parts of water-soluble solutes on the structure of water. When such molecules are brought into aqueous solution through a relevant solubilising group (e.g. sulphonate) then the water structure must change to accommodate the non-polar or hydrophobic residues. This change represents a gain in entropy for the whole system. Since most dyeing processes are restricted to aqueous systems, hydrophobic

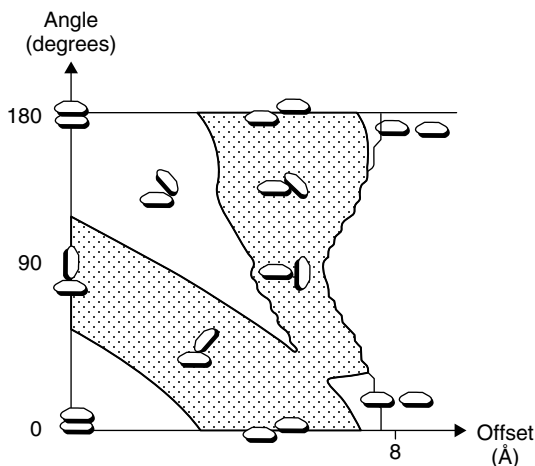
interactions are likely to play an important role in determining both dye uptake by fibres and subsequent wet-fastness. Zollinger¹² highlighted hydrophobic interactions as being responsible for over-dyeing effects on nylon as well as the unusually high substantivity of dyes containing bulky aryl or alkyl residues for wool.

Since dyes and fibres such as wool, silk and polyester both contain aromatic residues it is worthwhile to consider current thinking regarding π - π interactions. Hunter¹⁵ points out that such π - π interactions are commonly used to explain interaction between two or more aromatic molecules, but current evidence shows that they are negligible compared to electrostatics.¹⁷

At first sight it might be expected that, since aromatic groups are planar, maximum VDW interactions occur in a perfectly flat stacked arrangement. In water, hydrophobic interactions will also favour stacking, since the flat π -electron surfaces of the dye molecules are non-polar.¹⁸ Thus authors¹⁹ of papers on dye-aggregation in aqueous solution tend to draw the aggregates as perfectly stacked molecules with maximum overlap of free aromatic rings. Hunter and Sanders²⁰ have studied the geometry and energy contour plots of two stacked porphyrins and noted that the aromatic residues were in an offset or staggered arrangement. To explain these observations the above authors concluded that electrostatics provide a large repulsive force which pushes the π -systems away from the usually accepted maximum overlap position; the best model involved a positively charged σ framework sandwiched between two idealised ' π -atoms'. Continuing this analysis led Hunter¹⁵ to the conclusion that certain face-to-face arrangements of aromatic systems lead to repulsion and other arrangements such as face-to-edge and offset lead to attraction. He was thus able to construct a very useful diagram, which is reproduced in Fig. 1.5.

This new way of thinking about aromatic interactions¹⁵ allowed a ready explanation of the characteristic herringbone packing of aromatic hydrocarbons in the crystalline state²¹ and also explained the phenylalanine-phenylalanine geometries found in X-ray crystal structure analysis results from certain proteins.²² The maximum electrostatic attraction for two aromatic systems was subsequently calculated as 6 KJ mol⁻¹ which represents only a weak interaction. However, dyes are poly-aromatic systems and in fibres such as wool the aromatic side-chain residues in phenylalanine, tyrosine and tryptophan often occur in the same region; thus the overall small contributions, when summed, become significant.

Lewis²³ contends that the previous explanations of non-polar interactions in dye-fibre systems have tended to neglect the special case of aromatic interactions. Attention should be drawn to the anomaly that in aqueous systems hydrophobic interactions increasingly break down above about 60°C and many of the synthetic polyamide fibre over-dyeing phenomena

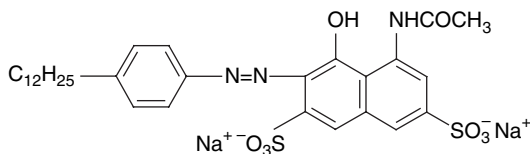


1.5 Electrostatic interactions between two benzene rings as a function of orientation.

are observed when dyeing in boiling aqueous solution. It is thus proposed that, rather than hydrophobic interactions, aromatic interactions are largely responsible for the over-dyeing effects observed when dyeing synthetic polyamide fibres with monosulphonated dyes.

1.3.3 Pathways to dye diffusion

An individual wool fibre has a very hydrophobic surface which if undamaged resists water penetration; it is thus difficult to imagine dye solution transport in a transcellular manner but rather intercellular diffusion seems more likely. The most widely accepted view regarding the pathway to dye diffusion, developed by CSIRO workers,^{24–26} is that the dye molecules pass rapidly through the heavily water swollen cell membrane complex (CMC) proteins, initially between the cuticle scales, and thence into the cortex. In one approach,²⁴ anionic metal-complex dyes were prepared using Pt, Pd and U as the complexing elements and dyed on to wool under a variety of conditions. These dyes could be located and mapped in the dyed fibres using Transmission Electron Microscopy (TEM) since, due to their high nuclear density, they have high electron scattering power. TEM analysis was able to show that these dye molecules entered the wool fibre between the edges of cuticle cells, then diffused into the non-keratinous endocuticle and CMC material, followed by diffusion to the inter-macrofibrillar material and the nuclear remnants; finally significant amounts of these dyes were associated with the more hydrophobic proteins of the A-layer in the exocuticle and with the high sulphur matrix proteins in the cuticle. Brady^{27,28} used fluorescence



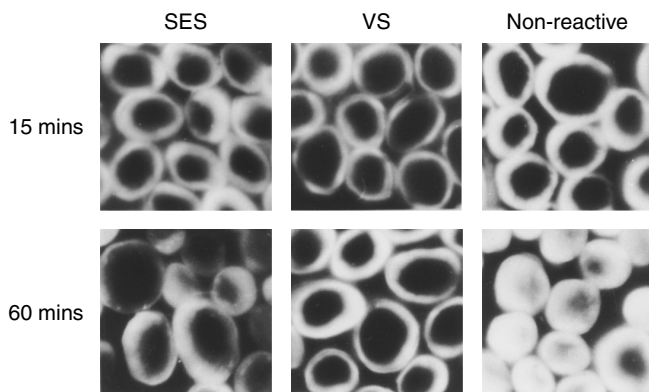
1.6 C.I. Acid Red 138.

spectroscopy to following the diffusion pathways of a fluorescent rhodamine dye (C.I. Acid Red 52) and came to very similar conclusions – reinforcing the above observations that dye diffusion occurs via the inter-cuticular, non-keratinous proteins into the fibre.

Fibre-reactive dyes show a different diffusion profile since they form covalent bonds and thus become immobilised much earlier in the above diffusion process than non-reactive dyes. Confirmation came from a study by Lewis and Smith²⁹ using a vinylsulphone derivative (VS), a sulphatoethylsulphone derivative (SES) and a non-reactive sulphanilic acid/hydroxytriazine derivative of a sulphonated di-amino-stilbene; these compounds act as fluorescent brightener models for reactive and hydrolysed dyes. The diffusion pathways of such colourless models when ‘dyed’ at the boil for different time periods could thus be followed using fluorescence microscopy; ultra-violet excitation at *circa* 340 nm resulted in the emission of intense blue visible light. In this way it was shown that the highly reactive free VS form did not penetrate far into the fibre but reacted with proteins in the endocuticle and the endocuticular intercellular regions; the less reactive SES form penetrated the fibre more deeply but was also mainly associated with the above regions; the non-reactive model gave full penetration of the fibres after dyeing for 1 h at the boil. Figure 1.7, taken from the original thesis,³⁰ shows these fluorescence-microscope results after dyeing 15 min and 60 min at the boil.

These are very important findings and demonstrate that the distribution of fibre-reactive dyes has to be very different to acid dyes without fibre-reactive residues (acid dyes, acid-milling dyes and metal-complex dyes). It is particularly significant that reactive dyes selectively covalently bond to and hence modify proteins in the CMC and endocuticular regions of the fibre; these chemical modifications may actually decrease the water-solubility of these proteins and hence favourably influence the loss of soluble wool proteins during aqueous dyeing at the boil.

The important question as to why the wool fibre cuticle surface does not allow transcellular diffusion of dyes was actually addressed prior to the above studies by such workers as Hall;³¹ the latter author proposed that dyes gain entry to the wool fibre interior via the junctions between the scales rather than directly through the scale surface. The presence of a barrier to dyeing at the scale surface is widely accepted (e.g. Rippon²⁶); the nature of



1.7 Fluorescence-microscope images of fibre cross-sections from wool 'dyed' with reactive/non-reactive dyes showing diffusion pathways after dyeing 15 mins and 60 mins at the boil.

this barrier has become the subject of intensive research since it is expected that a simple process to remove it would render wool more readily dyeable and printable – and possibly even more importantly readily shrink-resisted. Current evidence supports the thesis that the surface barrier is a proteo-lipid with the lipid being covalently bonded to the protein via a thioester linkage to cysteine.³² A simple process to remove the lipid would produce a modified fibre³³ which would be more readily dyed and printed, and even shrink-resisted, compared to the untreated fibre; chlorination does partially remove this surface lipid but its use may give rise to environmental problems related to the production and discharge of organo halogen pollutants. Rippon²⁶ has developed an amphoteric surfactant, Valsol LT or Sirolan LTD, for treating wool in a simple pre-scour prior to dyeing – since this treatment brings about some lipid removal the wool becomes more readily dyeable at 80–90°C. Chlorination with acid hypochlorite or chlorine gas (Kroy process) removes these surface lipids and oxidises cystine to cysteic acid; this process, usually accompanied by a cationic polymer after-treatment, is widely used for producing shrink-resist wool and also as a preparation process for wool printing. The cationic polymer has no affinity for untreated wool and its substantivity for chlorinated wool is a result of a combination of surface oxidation to give an anion-rich surface (cysteic acid formation from cystine disulphide oxidation) and the removal of the surface bonded lipids responsible for the hydrophobic properties of the wool fibre surface. Chief amongst these is 18-methyleicosanoic acid, which is covalently bound to the surface of the fibre via a thioester link at cysteine.

Perachem Ltd have patented a method for rapid removal of covalently bonded surface lipid which is currently being trialled.³⁴ In the Perachem process the first step is delipidisation with a selected nucleophile/surfactant

system which attacks the thioester linkage facilitating the removal and dissolution of the lipid from the wool. Delipidisation is achieved in less than 10 s and, as such, is consistent with the continuous processing speeds demanded by the industry. When the lipid is removed the treated wool exhibits a hydrophilic character and therefore 'wets out' instantly in water.

1.4 Environmental impact of wool colouration processes

1.4.1 Chrome dyeing processes

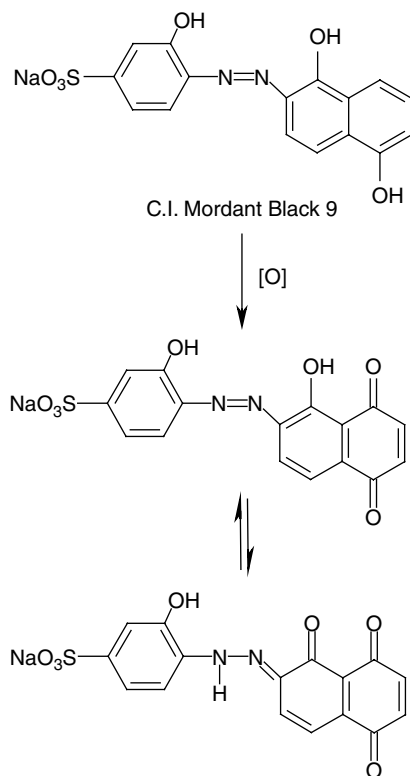
In order to achieve very black shades on wool chrome dyes have found widespread usage since they give the desired shade of black, coupled with outstanding wash- and light-fastness. It is interesting to note that the blackest blacks produced for the Japanese tuxedo market are invariably produced by dyeing chrome dyes on chlorinated wool. It has been estimated that chrome dyes still account for some 20% of the total wool dye market, predominantly for dyeing black and navy blue shades. Invariably the dyeing is after-treated with sodium dichromate to produce the metal-complex dye in the fibre. It is the toxicity of Cr(VI) which should give rise to concern both from the point of view of its effect on worker's health and its effect in the environment following discharge of exhausted dyebaths. Cr(III) is relatively safe, it is naturally present in soils and is even considered an essential human dietary component. If Cr(III) could be used to complex the ligands in the dye, then chrome dyeing would be a much more environmentally friendly procedure.

The Cr(III) cation cannot be applied directly as the chroming agent as under the acidic conditions used in dyeing it has low substantivity for the positively charged, protonated wool fibre. However the trivalent chromium cation can be readily converted to an anionic complex by reaction with suitable colourless ligands; such complexes have substantivity for wool under hot acidic conditions. The complexes must not be too stable since the carrier ligands have to readily exchange the chromium with the ligand groups in the dye. Suitable complexing compounds include α -hydroxycarboxylic acids such as lactic acid and salicylic acids, and polycarboxylic acids such as maleic acid.³⁵⁻⁴² Much of the published work has focused on lactic acid³⁵⁻³⁹ and 5-sulpho-salicylic acid.^{40,41}

An important factor to be taken into consideration when replacing Cr(VI) with anionic Cr(III) complexes is the oxidising effect of the dichromate anion. During after-chroming dyed wool with dichromate, absorbed Cr(VI) is reduced by the wool fibre to a Cr(III) species which complexes with the dyestuff to give full rich shades of excellent wet-fastness. The exact nature of the oxidising effect of dichromate is not fully understood, but it has been

shown that in order to produce equivalent dyeings with the Cr(III) complex system a substantial amount of an oxidising agent (usually hydrogen peroxide) must be added during the chroming stage to effect full shade development and to produce dyeings of the expected wet-fastness. The amount of hydrogen peroxide required is influenced by the dye used; in some cases the dye molecule itself should be oxidised to give the expected chrome-dyed shade as is the case when dyeing with C.I. Mordant Black 9 (Diamond Black PV – DyStar).³⁹ This oxidation process is shown in Fig. 1.8.

Xing and Pailthorpe have described the use of the anionic complex prepared from 5-sulpho-salicylic acid and chromic sulphate⁴⁰ for after-chrome dyeing of wool and have recently further developed the method for the industrial processing of cashmere fibres.⁴¹ To achieve the correct shade and wet-fastness properties these authors proposed the addition of a small amount (0.6% on mass of fibre, o.m.f.) of Cr(VI) to the after-chrome process 5 min after the addition of the Cr(III) complex. The structure of this latter complex was not revealed, simply being coded SCA-Cr; this addition of



1.8 Oxidation of Diamond Black PV (C.I. Mordant Black 9).

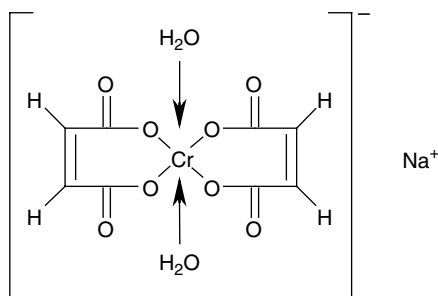
Cr(VI) can be interpreted as an oxidation step. Lewis *et al.*⁴² have described an after-chrome dyeing system using sodium maleate as the preferred complexing agent for Cr(III) cations and oxidation at the end of the after-chroming process with hydrogen peroxide.

The maleate complex was readily prepared by dissolving maleic anhydride (18.7 g) in water (100 mL) and the solution boiled for 5 min then cooled; this solution was neutralised using solid sodium carbonate (20 g); chrome alum (48.4 g) was dissolved in water (200 mL), this solution was added to the sodium maleate solution and the volume was made up to 500 mL with water; boiling for 5 min ensured complex formation (ligand: chromium = 2.1). When dyeing 1 kg of wool, 500 mL of this solution should be added to the dyebath at the after-chrome stage giving a Cr factor of 0.35. The nature of the complex is shown in Fig. 1.9.

From this work⁴² the following chrome dye application process was developed:

Dyeing was carried out in a 1 kg Obermaier sample package dyeing machine. The bath, containing 1 kg of wool yarn wound on a package, was set at 50°C at a liquor to goods ratio of 16:1, and at pH 4.0; chrome dye was added, the bath raised to the boil over 40 min and maintained at the boil for 1 h. The temperature was then lowered to 80°C and the appropriate amount of Cr(III)/maleate complex added; the pH was adjusted to 3.5–4.0 with formic acid and the bath returned to the boil. After 15 min hydrogen peroxide (65 mL of 35% w/w material) was added and after another 15 min a further 65 mL H₂O₂ (35%) was added; boiling was then continued for a further 25 min. The dyed package was washed off for 20 min at 50°C (pH 8.0 with ammonium hydroxide, 1 g/L 0.880 NH₃); final rinsing with dilute acetic acid (pH 5) at 40°C completed the process.

For comparative purposes the following standard chrome dyeing process was carried out. In this case the first dyeing stage was as described but the after-chrome process was performed by cooling the dyebath to 80°C and



1.9 Maleic acid/Cr(III) complex with Na⁺ counter ion.

adding the requisite amount of dichromate (for 4% o.m.f. Diamond Black PV (200%) a Bayer G Cr factor of 0.35 was used); the bath was returned to the boil and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) added ($1.7 \times$ mass of $\text{K}_2\text{Cr}_2\text{O}_7$ used). Boiling was continued for a further 30 min.

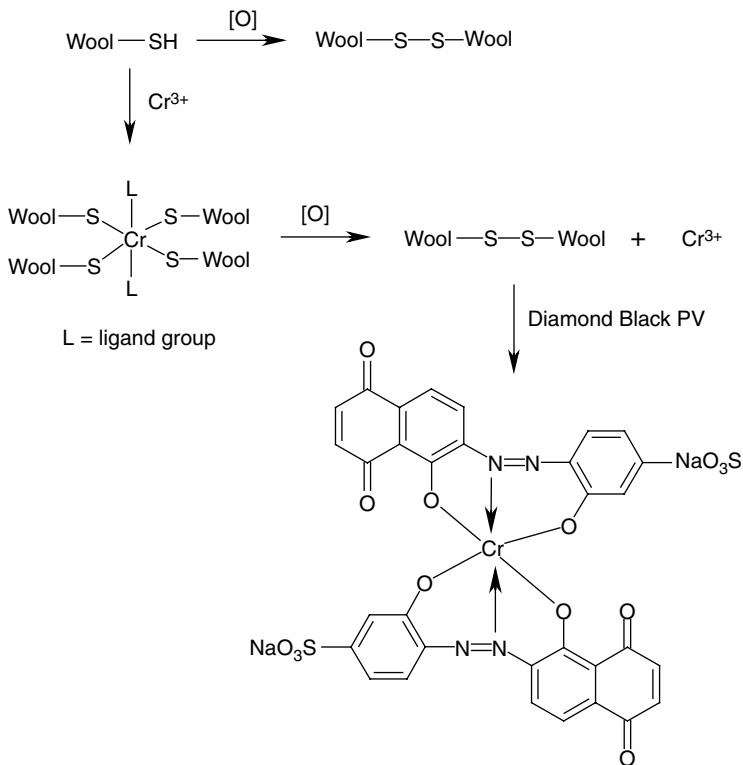
In the case of those dyes which do not change structure on oxidation, for example, Diamond Fast Bark Blue RRN (C.I. Mordant Blue 9) and Diamond Fast Bordeaux BL (C.I. Mordant Red 30), the total amount of peroxide required for a 1 kg package dyeing must be reduced to 120 mL of 35% H_2O_2 . The requirement to add peroxide is necessary to produce dyeings having a wet-fastness level comparable to those dyeings produced with the usual dichromate process. In particular, potting fastness tests critically distinguish the non-peroxide after-treated samples.

It was proposed that the necessity to use oxidising agents to achieve the maximum wet-fastness properties from the Cr(III)/maleate system is due to the strong binding of Cr(III) to thiol ligands. During dyeing of wool at the boil significant setting occurs due to thiol-disulphide interchange reactions;⁴³ undoubtedly the small amount of cysteine free thiol (*circa* 39 μmoles per kg of wool) undergoes β -elimination to produce dehydroalanine and H_2S . The latter attacks intact disulphides to produce further free thiols, initiating a chain reaction which produces significant permanent set. There is thus a significant concentration of free thiols in the wool at the end of the dyeing cycle which, being highly nucleophilic, selectively binds the chromium when the Cr(III) maleate complex is introduced. An oxidant is thus necessary to free the chromium from this thiol ligand binding in order to make it available for complex formation with the dye. Figure 1.10 summarises this mechanism.

If oxidation in the after-chrome cycle re-forms toxic Cr(VI) then these research results would not be too useful practically. Thus the sensitive diphenyl-1-carbazide colour test for Cr(VI) formation was carried out on residual dyebaths from dyeings produced by the new process; no positive results were seen. However, when peroxide oxidation of the Cr(III) complexes was carried out under alkaline conditions, clear evidence for Cr(VI) formation was seen.

Chromium content of residual dyebaths

Analysis by Atomic Absorption Spectroscopy indicated that the effluent obtained from the Cr(III) complex dyeings contained considerably higher concentrations of residual chromium than the dichromate standards. However, a significant reduction in the concentration of residual chromium may be achieved by a reduction of the Cr factor when using the Cr(III)/maleate system (Table 1.2). Trials have shown that the Cr factor may be reduced to 0.20 without affecting the shade or fastness to potting. Reduction



1.10 Proposed mechanism for the action of hydrogen peroxide in the Cr(III) maleate complex chroming system.

Table 1.2 Residual chromium levels in effluent from 4% o.m.f. Diamond Black PV (200%) dyeing with varying Cr factors

Cr Factor and method	Chromium level detected in effluent (mg/L)
0.35 dichromate-thiosulphate standard	12.0
0.35 Cr(III) complex	104.0
0.25 Cr(III) complex	53.6
0.20 Cr(III) complex	32.8
0.175 Cr(III) complex	24.6
0.15 Cr(III) complex	12.3
0.12 Cr(III) complex	11.5

of the Cr factor to lower than 0.175 leads to poor chroming and inadequate shade development.

Further reduction in the chrome content of the effluent was achieved by fresh bath chroming. King and Brady^{44,45} have attributed this effect to

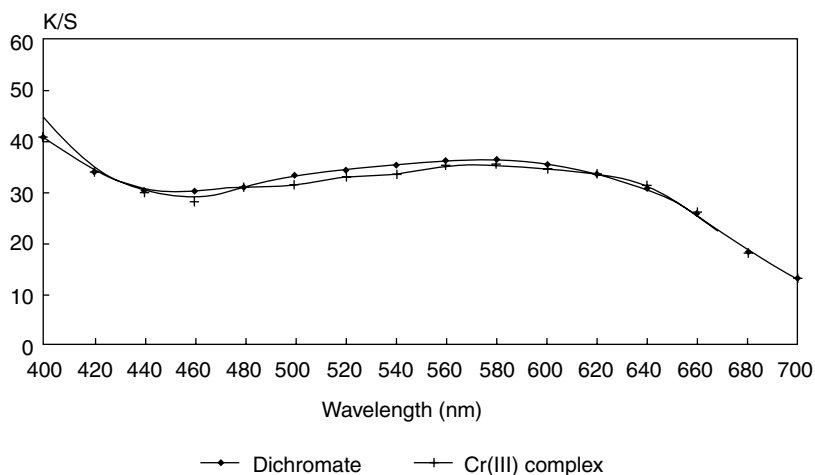
the reaction of dichromate with soluble protein in the after-chrome bath. Rinsing, prior to after-chroming, will remove residues of dye and soluble protein which could compete in the bath for the Cr(III) complex. Amino acid residues such as aspartic acid, glutamic acid, cysteine and histidine will form strong complexes with Cr(III).

The reflectance spectra of 4% o.m.f. dyeings of Diamond Black PV chromed by the standard and the new Cr³⁺ maleate method were taken and K/S values calculated. Figure 1.11 reproduces these spectra and it is clear that the colour yields of the two processes are very similar.

1.4.2 Absorbable organo halogens (AOX) in wool dyeing and finishing effluents

Special attention is required when discharging compounds containing AOX. The concept of AOX has arisen from a German drinking water directive (DIN 38409414 – 1985). Consent limits as low as 2 mg/L have been applied.

Products used by the dyer and printer which fall into this category are the insect-resist agents applied to wool in dyeing, some types of carriers for disperse dyeing polyester, certain chromophores themselves and some halogen-containing classes of reactive dyes. This type of foreseeable legislation will therefore direct the colour chemist to develop new systems that will reduce these discharges to the allowable limits. These implications are indeed far-reaching. For example, in the case of reactive dyeing cellulosic fibres, the demand for achieving virtually 100% dye uptake and covalent



1.11 K/S spectra for Diamond Black PV, using standard dichromate and the chrome maleate complex (fresh bath chroming methods).

bonding is urgent. Research is therefore required as to whether to develop innovative reactive systems or to develop fibre pre-treatments that solve the problem of existing reactive dyes.

It is worthy of note that dyeing chlorinated wool leads to effluents containing on average more than 1000 mg/L AOX. So far special dispensation, to discharge this concentration of AOX, has been given to dyers of machine-washable wool produced by the chlorine–Hercosett (TM Hercules Powder Corporation) continuous top process. An important research activity is the production of machine-washable wool using non-chlorine procedures. In fact there is renewed urgency in this area as expected EU directives are likely to force processors to abandon the chlorination route.

AOX-free shrink-resist finishing

Currently the most popular method to produce machine-washable wool tops is the so-called chlorine–Hercosett process. The chlorination pre-treatment removes much of the covalently bound lipid material from the wool surface and also oxidises surface cystine disulphides to cysteic acid; these effects cause the fibre surface to become both hydrophilic and anionic and highly receptive to the cationic polymer, Hercosett, which ‘exhausts’ and spreads onto the surface of each individual fibre.

Alternative systems for preparation of the fibre surface for shrink-resist treatments based on peroxide chemistries have been explored but to date have not realised the same commercial success as the chlorine–Hercosett process. Most studies have in fact explored the potential of Caro’s salt ($\text{KHSO}_4\cdot\text{KHSO}_5$) as a direct chlorine replacement⁴⁶ but in this case it is vital to include a sodium sulphite treatment not only to remove excess oxidant but to generate sufficient shrink-resistance; undoubtedly this system produces anionic polypeptides at the fibre surface by a process of oxidative sulphytolysis⁴⁷ to give cysteine-S-sulphonate (wool Bunte salt) as the hydrophilic anionic residues. In continuous processing this technique has not allowed the application of Hercosett polymer, presumably because removal of covalently bonded lipid is inefficient compared to chlorination processes. Other workers⁴⁸ have trialled permonosulphuric acid/sulphite followed by silicon polymer application in an attempt to redress the above problem; unfortunately silicon polymers lead to subsequent problems in spinning and dyeing.

It is something of a hindrance, and an extra cost to be borne by the processor, that a separate process has to be carried out to shrink-proof wool, usually prior to dyeing. The author has reported on a possible system⁴⁹ to achieve these objectives; this system involved the co-application, in a pad-batch fabric dyeing process, of a tri-functional Bunte salt-acetoxypolyol, with reactive halo-s-triazine reactive dyes. Providing that urea

and sodium bisulphite were also present in the pad-liquor, excellent dye fixation and level dyeings were obtained – the fabrics were also machine washable and possessed a good soft handle. The Bunte salt ‘capped’ polyol is water soluble and surface active; reaction with wool thiol groups converts it to a cross-linked poly-disulphide-polyol which is water insoluble and imparts the shrink-proofing effect via fibre-fibre spot welding.

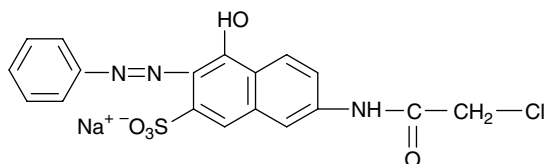
1.5 Reactive dyes for wool

The chemistry of reactive dyes for wool has been fully reviewed^{50,51} but the most important features will be detailed here.

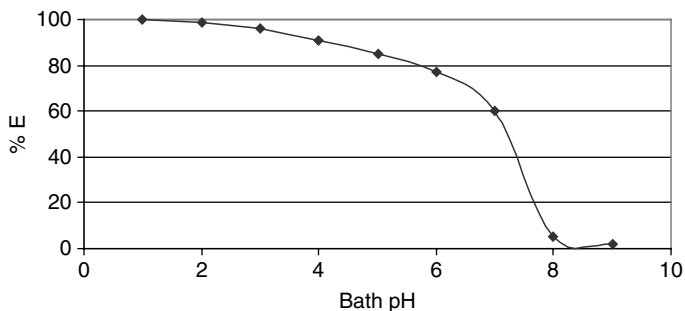
Studies on wool were of great significance in the early development of reactive dyes. In particular the ω -chloroacetyl amino reactive group appeared as early as 1938 in the IG dye, Supramino Orange R (Fig. 1.12).

Lewis *et al.*^{52,53} showed that the plot of pH versus uptake of the above dye on wool was quite different from a normal acid dye (e.g. Fig. 1.4); these results are reproduced in Fig. 1.13.

A study of this figure shows that the covalent reaction with nucleophilic sites in the fibre is promoting significant uptake of dye even at pH 6 (80% E); non-reactive analogues give about 1–5% E values at this pH value.



1.12 Supramino Orange R.

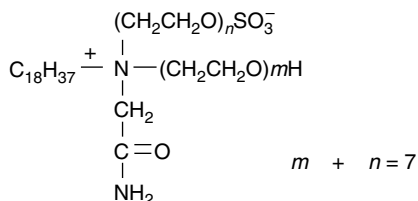


1.13 Uptake of ω -chloroacetyl amino reactive dye on wool versus bath pH.

Ciba put together a small range of bright wool dyes containing this grouping in 1954 (Cibalan Brilliant). In 1952, following the patented work of Heyna and Schumacher,⁵⁴ Hoechst marketed Remalan and Remalan Fast, 2:1 pre-metallised reactive dyes for wool which contained pendant sulphatoethylsulphone residues capable of elimination to vinylsulphone reactive groups when applied from boiling dyebaths above pH 5. Hoechst even sold chrome dyes with the sulphatoethylsulphone residue being incorporated in the dye molecule, these being Metachrome Orange H-3R, Metachrome Gey RL, Salicinchrome Orange H-3R and Salicinchrome Grey RL. However, it seemed that the marketing push for selling these dyes as fibre-reactive systems was somehow lacking, probably because wool had only a small share of the textile fibre market. It was only when developments took place which allowed covalent fixation of dyes on the major textile fibre, cotton, that a major marketing effort commenced to sell the reactive dye concept for wool dyeing.

Also it should be noted that the above early reactive dyes for wool gave considerable problems of unlevel dyeing, especially in piece dyeing and yarn hank dyeing; thus their usage was mainly in the fields of loose wool stock and wool top dyeing. A major advance in reactive dyes for wool occurred in 1966 with the launch of the Lanazol dyes (Ciba-Geigy); these dyes were based on the α -bromoacrylamido group⁵⁵ and were sold with the very important level dyeing auxiliary, Albegal B. Albegal B is an amphoteric product which, according to Datyner and Christoe,⁵⁶ possibly has the following general structure (Fig. 1.14).

It is noteworthy that dyeing in the presence of this novel product alleviated the problems of unlevel dyeing associated with reactive dyeing of wool. By happy coincidence the launch of the Lanazol dyes coincided with the marketing of truly machine-washable wool, produced by the continuous chlorine–Hercosett treatment of wool tops, a process developed by scientists at CSIRO and IWS.⁵⁷ Other companies followed suit, Bayer and Sandoz launching difluoro-monochloro-pyrimidine dyes (Verofix/Drimalan F)⁵⁸ and Hoechst launching a reassembled range of ‘blocked’ vinylsulphone dyes (Hostalan).⁵⁹ Dyeings produced on the chlorine–Hercosett treated substrate with acid dyes, acid-milling dyes and pre-metallised dyes did not



1.14 Typical amphoteric levelling agent used in wool reactive dyeing.

show adequate wash-fastness properties but dyeings produced with reactive dyes gave outstanding washing performance.⁶⁰

1.5.1 Modern reactive dye systems for wool fibres

In light of increasing environmental concerns with heavy metals it is desirable to use reactive dyes to match deep shades of black and navy blue in order to offer the dyer a real alternative to chrome dyes. In this context dye manufacturers have increased their efforts to offer wool dyers ranges of attractively priced reactive dyes; examples include Lanazol CE dyes from Ciba, Realan dyes from DyStar and Drimalan dyes from Clariant. Black and navy blue shades are often based on the popular and widely available dye, C.I. Reactive Black 5. This dye is a bifunctional reactive dye since it contains two sulphatoethylsulphone residues, which activate to vinylsulphone on boiling at pH 5.5.

Müller⁶¹ has reviewed the nature and amount of AOX residues in textile effluents; various reactive dye systems such as halo-triazines and halo-pyrimidines can give problems and AOX discharges can be reduced by selecting dyes containing only sulphatoethylsulphone residues as the reactive group.

1.6 Wool protection during dyeing by using reactive dyes and/or anti-setting agents

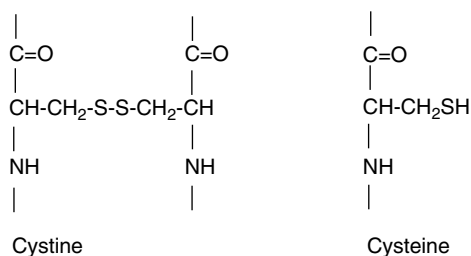
Permanent setting is a contributory factor leading to loss in wool fibre strength during dyeing. It is the main cause of increased hygral expansion of wool fabrics following piece dyeing, and is also the reason for surface marks such as ‘crow’s-feet’ in piece dyeing and the source of reduced bulk or yarn leanness following package dyeing.^{62–64} Apart from the above wholly negative effects, permanent setting can sometimes be seen as beneficial: such instances include the setting of wool yarn in hank form when using hank dyeing machines – this gives extra bulk and resilience to yarns and explains why this dyeing route remains popular for the production of dyed yarns for wool carpet manufacture. It is helpful to summarise the various chemistries involved in the production of permanent set in wool dyeing.

Wool is a heterogeneous material made up of keratin proteins, a small amount of non-keratinous proteins and even smaller amounts of lipid and fatty acid materials. The keratinous or cystine disulphide cross-linked proteins are responsible for most of wool’s physical properties and thus the reactivity of the cystine disulphide residue is of paramount importance. The cystine content of wool varies but an appropriate average value is $450 \mu\text{mol}\cdot\text{g}^{-1}$ and for its reduced form, cysteine, $30 \mu\text{mol}\cdot\text{g}^{-1}$. The chemistry

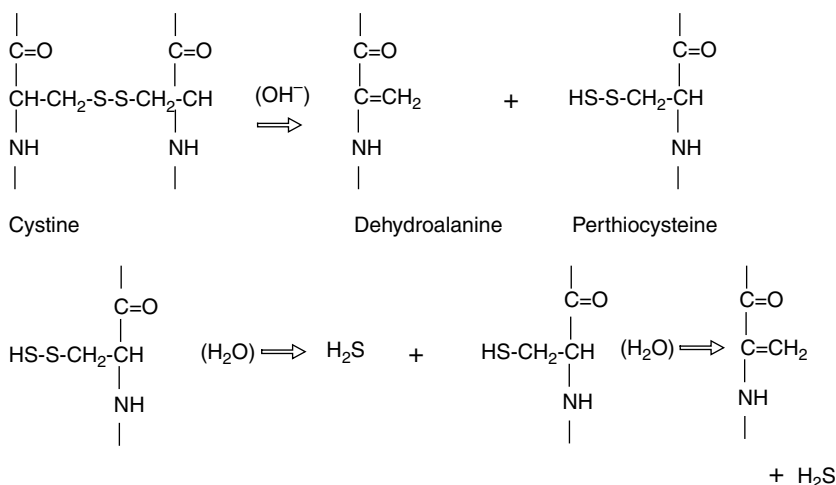
of these residues bound to the protein chains through the amide linkage is illustrated in Fig. 1.15.

Both these amino acid residues can readily undergo a *trans* 1,2- β -elimination reaction to form the dehydroalanine residue which contains an activated double bond capable of subsequent Michael addition with suitable nucleophiles. These reactions occur in water; the extent and nature of the reaction depends especially on the parameters pH, temperature and time.⁶⁵⁻⁶⁷ The reactions are activated by the electron withdrawing character of the adjacent amide carbonyl residue. In general the thiol form, cysteine, more readily undergoes β -elimination than the disulphide form, cystine; even at pH 3, in boiling aqueous dye baths, there is some elimination of hydrosulphide ion from the cysteine residue whereas the cystine disulphide only undergoes such reactions above pH 7. Figure 1.16 summarises these reactions.

The hydrogen sulphide or hydrosulphide anion produced in the above reaction is capable of ready reaction with cystine disulphide



1.15 Representation of bound cystine/cysteine in wool keratin.



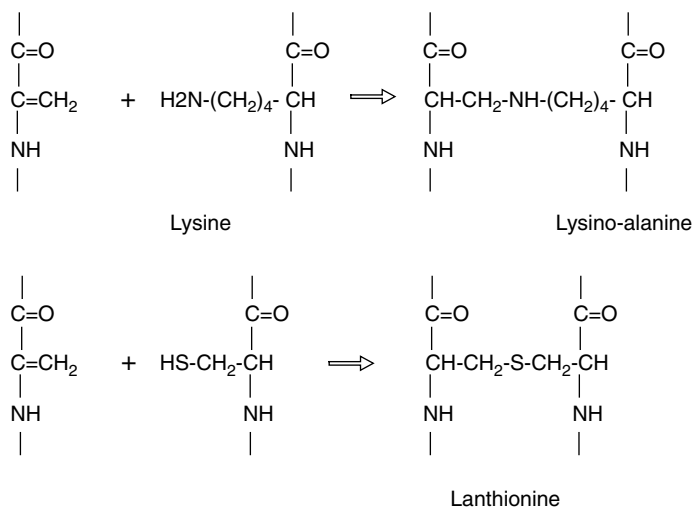
1.16 Elimination reactions of cystine and cysteine.

residues to produce further cysteine thiol residues which will undergo rapid β -elimination to dehydroalanine and hydrogen sulphide in boiling dyebaths; this is clearly the start of a runaway degradation reaction. The reactive entity, dehydroalanine, will undergo Michael addition with amino nucleophiles present in histidine and lysine residues and with thiol nucleophiles present in cysteine; in this way, more stable cross-links such as histidino-alanine, lysino-alanine and lanthionine are formed.^{68,69} The extent and exact composition of these new cross-linking amino acids varies greatly with pH and temperature of treatment, since the nucleophilicities of amino and thiol residues become greater as pH and temperature increase. The chemistry of these cross-linking reactions is exemplified, for lysine and cysteine residues, in Fig. 1.17.

The above cross-links will not undergo degradation or elimination reactions under conditions normally encountered in wool dyeing and are thus likely to be of great importance in explaining the phenomena of permanent setting during wool dyeing. Also of some importance in setting is the so-called thiol-disulphide interchange reaction.^{70,71}

It is clear from the above discussion that control of setting in dyeing can be achieved by the addition of chemicals which scavenge hydrosulphide anions as they are liberated or which rapidly modify free cysteine thiol residues to prevent the elimination reaction; in practice this can be achieved in two ways:

- inclusion of oxidants in the dyebath; and
- inclusion of fibre-substantive electrophiles in the dyebath.

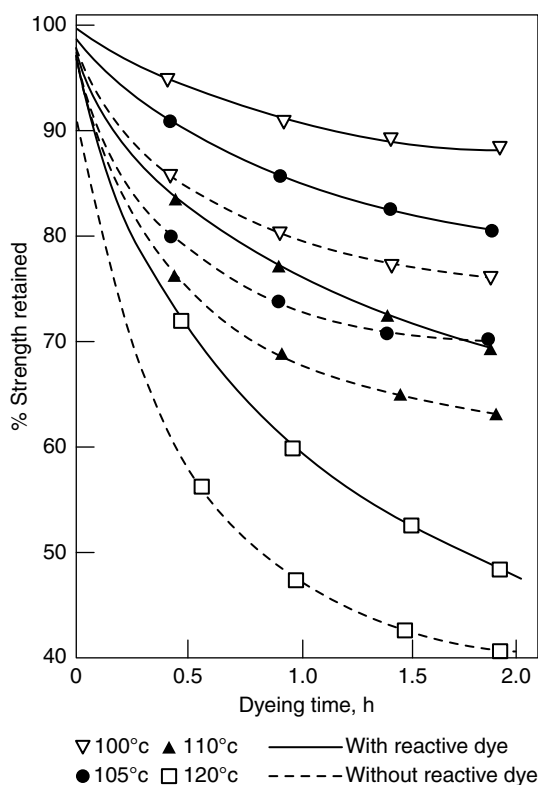


1.17 Formation of lysine-alanine and lanthionine cross-links.

It is thus important to measure set following dyeing and most of the published research in this area uses K pke's crease angle method to achieve this;⁷² typically blank dyeings of wool fabric in pH 5 buffer for 1 h at the boil, without anti-setting agent present, give set values of *circa* 70%, whereas including an effective anti-setting agent gives a set value of *circa* 30%.

Reactive dyes, dyed in moderate to heavy depths of shade, actively prevent damage in wool dyeing⁷³ especially those dyes which contain activated carbon-carbon double bonds and which thus react with fibre nucleophiles via a Michael addition mechanism (these dyes include acrylamido dyes and vinyl-sulphone dyes). The magnitude of this effect increases with increasing amounts of reactive dye applied being optimum at *circa* 3% dye o.m.f. The importance of this effect when dyeing wool fabric at pH 4 with the α -bromoacrylamido reactive dye, Lanazol Red 6G – 4% o.m.f., is demonstrated in Fig. 1.18.

It is interesting to consider why reactive dyes based on reactive halogenated heterocycles, which react with wool fibre nucleophiles by a nucleophilic substitution reaction, are less effective in controlling wool damage in dyeing than are the activated carbon-carbon double bond type of reactive



1.18 Effect of dyeing time and temperature on wool fabric strength.

dye. From the above discussions it is clear that successful control of damage and set go hand-in-hand and it is thus necessary to look carefully at the reactivity/stability of the reactive dye-cysteinyl residue covalent bond. Thioether derivatives of triazine or pyrimidine heterocycles will react further with amines to form bonds of greater stability; the leaving group in this reaction being the substituted thiol.⁷⁴ The thioether formed from reaction with an activated carbon-carbon double bond is, however, resistant to nucleophilic attack or β -elimination under the mildly acidic conditions pertaining in wool dyeing.⁷⁵

When set was measured from dyeings on wool fabric produced at pH 5 from the activated halogenated heterocycle type of reactive dye, Drimalan Red F-2G – Clariant (3% o.m.f.), a value of 74% was obtained; in contrast when the above dye was replaced with a reactive dye containing an activated carbon-carbon double bond, Lanazol Red 6G – CIBA (3% o.m.f.), a set value of 41% was obtained.⁷⁶ The reactions responsible for these differences are summarised in Fig. 1.19.

The importance of hydrogen sulphide as a catalyst to promote setting/wool damage under dyeing conditions was proven by Lewis and Smith⁷⁷ who demonstrated that a bis-(dye-sulphonyl ethyl)-thioether dye was present in the bath after dyeing with a model vinylsulphone dye. This dye arises from the reaction of the vinylsulphone with free hydrogen sulphide, according to the mechanism shown in Fig. 1.20.

1.6.1 The role of oxidants to prevent setting in dyeing

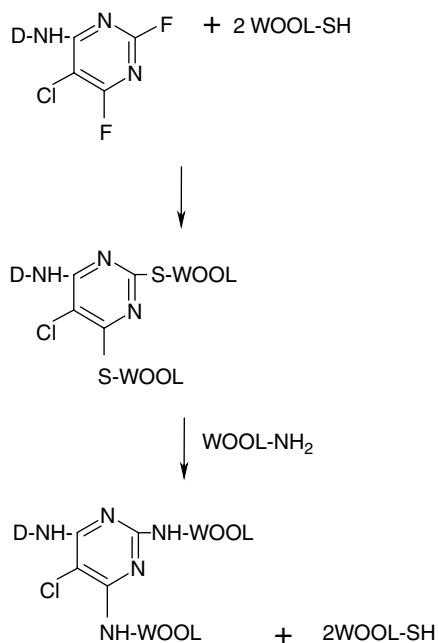
One of the most useful anti-setting systems for use in wool dyeing was developed by workers at CSIRO, IWS and BASF.⁷⁸ This system, offering improved fibre physical properties, was based on a mixture of hydrogen peroxide and a special auxiliary Basolan AS; the latter auxiliary performed two functions:

1. inhibition of the degradative effect of hydrogen peroxide on some wool dyes; and
2. enhancement of the stability of the oxidant in the boiling dyebath.

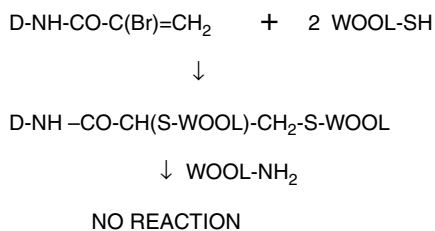
The BASF/IWS/CSIRO process⁷⁸ recommended dyeing wool in the presence of hydrogen peroxide (35%) at a level of 1 mL/L (minimum 2% on o.m.f.) and Basolan AS at 0.5 g/L (minimum 1% o.m.f.).

Kim and Lewis⁷⁹ studied the effect of hydrogen peroxide concentration on set after boiling wool fabric for 1 h at pH values 3, 5 and 7 in the presence of citric acid/phosphate buffers (McIlvaine buffers); their results are reproduced in Fig. 1.21.

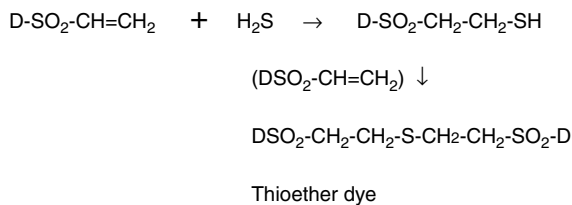
Activated heterocycle dye:



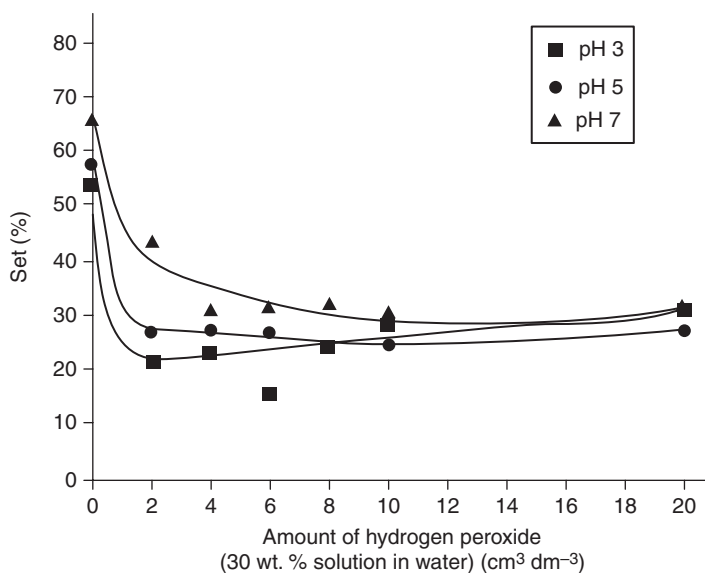
Activated carbon-carbon double bond dye:



1.19 Cysteinyl reactions with active heterocyclic and double bond types of reactive dye.



1.20 Thioether dye formation in wool dyebaths.



1.21 Plot of % set after boiling wool, at pH values 3, 5 and 7, with H₂O₂.

Hydrogen peroxide (30%) concentrations as low as 2 cm³dm⁻³ gave set values of 21% at pH 3 (control without oxidant gave 56% set), set values of 27% at pH 5 (control 59%) and set values of 43% at pH 7 (control 67%). The effect of pH on set parallels the effect of pH on cystine degradation; if the mechanism is β -elimination of cysteine as shown in Fig. 1.19, then a higher concentration of oxidant should be more effective at controlling set at pH 7 where elimination is more rapid – Fig. 1.21 confirms this hypothesis since 4 cm³dm⁻³ hydrogen peroxide gives the best control of set. The oxidant clearly functions by rapidly oxidising cysteine back to cystine or cysteic acid; of possible equal importance is the oxidation of hydrogen sulphide to bisulphate anion thus removing this reactive reducing nucleophile from the system.

Kim and Lewis⁷⁹ used FTIR second derivative spectroscopy to follow the production of cysteic acid when treating wool at the boil with hydrogen peroxide (0–10 cm³dm⁻³); by measuring the sulphonate band intensity, attributed to cysteic acid, at 1040–1044 cm⁻¹ it was shown that over-oxidation to cysteic acid was most significant in those treatments carried out at pH 7.

Other oxidants shown to have anti-setting properties include sodium bromate and sodium tetrathionate.⁸⁰

It is not possible to use oxidants such as hydrogen peroxide when dyeing with reactive dyes since the perhydroxy anion is a potent nucleophile which reacts at the electrophilic site in the reactive dye to rapidly produce the hydrolysed, inactive dye.

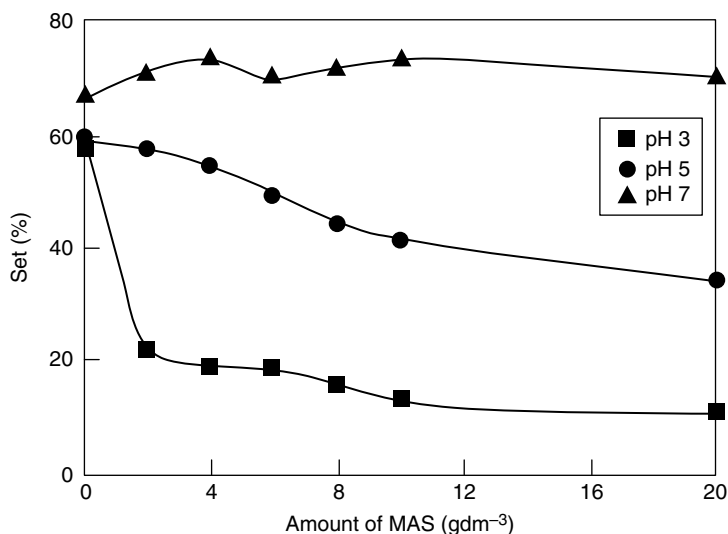
1.6.2 The role of electrophilic reagents to control setting in dyeing

At the same time as the hydrogen peroxide based Basolan AS-A system was launched, a system based on application of an electrophile Basolan AS-B was also marketed but the structure of the latter reagent remains undisclosed.

Kim and Lewis⁸¹ showed that sodium maleate (MAS) was a very effective anti-setting agent when included in boiling pH 3 wool dyebaths and their results are reproduced in Fig. 1.22.

This figure clearly demonstrates that the maleate anion is most effective at controlling set at pH 3; it shows only modest effect on set at pH 5 and has no effect on set at pH 7. The reason for this strong pH dependence lies in the modest substantivity of the maleate ion for wool under acidic conditions and its almost total lack of substantivity at pH 7 and above. It was estimated,⁸¹ from capillary electrophoretic analysis of the treatment baths, that when using 2 g/L sodium maleate for the 1 h boiling treatment, maleate anion uptake was 22% at pH 3, 15% at pH 5 and 4% at pH 7. The mechanism whereby maleate anions reduce the extent of wool setting in boiling aqueous treatments is described in Fig. 1.23.

Liao *et al.*⁸² synthesised N-naphthylmaleimide and showed it inhibited wool setting and also protected the wool component of a wool/polyester blend from serious damage during the high temperature dyeing step



1.22 Plot of % set after boiling wool, at pH values 3, 5 and 7, with sodium maleate.

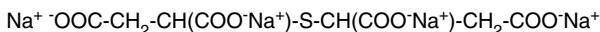
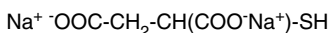
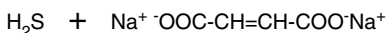
Reaction with wool cysteinyl residues:



Cysteine residue



Reaction of non-absorbed maleate with H_2S in solution:



1.23 Addition reactions of maleate with cysteinyl residues and H_2S .

required to adequately dye the polyester component with a disperse dye. These authors and others⁷⁸ attribute the main cause of setting, hence wool damage, in hot aqueous wool treatments to the thiol-disulphide interchange reaction without implicating cysteine residue β -elimination reactions.

1.7 Ink-jet printing of wool fabrics

Printing of wool fabrics has always been a small-lot, high fashion activity; this has meant that wool printing did not sit easily in print mills equipped with high productivity rotary screen printing machines capable of printing speeds of 50 m per minute. However, even in the cotton fabric printing industry runs of 500 m are now common and likely to become even smaller. Drawbacks of rotary screen printing methods include low machine utilisation efficiency or downtime; a pattern set-up can take 1 h and screen washing and drying processes can take 1–2 h. Also of concern is the time delay from print design to screen commissioning and screen delivery; this can be 3 or 4 weeks. Given the demands for individual designs it could be that the age of mass production printing to a particular colour-way and design is coming to an end; the only way to meet this challenge is to develop digital printing processes for textiles. Successful development of these digital systems will advantage wool and wool-blend fabric printers with their traditional small-run production. Digital printing eliminates the screen costs, allows designers

to make pattern and colour changes immediately and eliminates registration problems when printing.

Two issues are important before digital printing can commence commercially on wool fabric; the availability of suitable machinery and the formulation of fabric pre-treatments and ink formulations designed to give maximum colour yield, eliminate background yellowing and allow production of prints of high wet- and light-fastness.

1.7.1 Ink-jet printing machinery

Drop on demand ink-jet heads use either thermal or piezoelectric technology to deliver droplets to the substrate as needed. Thermal ink-jet heads have been the most popular for paper printing; they operate by thermally producing a bubble of water-based ink which is jetted out of the nozzle. High resolution prints are produced due to the small drop size and up to 1440 drops per inch covering can be obtained.

Piezoelectric ink-jet heads rely on an electric charge pulse to warp the interior of the ink chamber thus forcing the drops out of the nozzle. Piezo heads are seen as more robust and more suited for high volume printing; additionally it is envisaged that even pigment and binder compositions could be printed from such heads.

Continuous ink-jet printing machines are also being trialled; these machines use a continuous stream of charged ink droplets which passes through a deflection region where they are either directed onto the substrate or returned to the reservoir by deflection into a gutter. It seems likely that this system will be most capable of meeting the production speeds ultimately required to move ink-jet printing of textiles from a mainly sampling activity into mainstream production.

Examples of machines currently on the market are the CIBA (now Huntsman)- Reggiani Dream machine, the Mimaki TX 1600, Aristri (DuPont), Sophis Silk Express, Chromojet (Zimmer) and Encad TX150; these are all based on the piezo system. The most successful full-scale production machine is the Dream system. In terms of the sampling market the Mimaki systems seem to dominate; these are based on piezoelectric heads. The Mimaki TX is mainly used for sampling, giving 720 dots per inch coverage, and the TX2 wide-format machine (1.6 m) is used for small production and fast sampling. The Mimaki machines are sold with a 1 year warranty which requires sole use of Mimaki ink; replacement ink cartridges cost about £60 for 220 mL of ink. Each cartridge has a chip that monitors ink level and polices cartridge use. Clearly there is a totally new philosophy of colour purchase being developed by some printing machine manufacturers which could detract from rapid development of the textile ink-jet printing field.

1.7.2 Print pre-treatments and ink formulations

Fabric pre-treatment for ink-jet printing is seen by many as requiring a different approach compared to the requirements for screen printing. Thus there is already an established business activity in which fabric is prepared by simply padding and drying thickening agent; in the case of cotton ink-jet printing with reactive dyes an alkali such as sodium carbonate is also included in the preparation.

Wool preparation may be Kroy chlorination but on steaming potentially unacceptable levels of yellowing are produced. In the case of wool and cotton fabric ink-jet printing the author holds the strong opinion that reactive dyes should be the product of choice; they offer the potential of giving prints of excellent wash-fastness and minimal wash-off providing conditions that are optimised to achieve high fixation. Dye manufacturers offer ranges of high purity reactive dyes by desalting commercial products, thus maximising solubility; for deep shades inks may have to contain up to 200 g/L of dye in aqueous solution. The latter may be difficult to sustain over a period of time without aggregation, precipitation and subsequent jet clogging; this problem was virtually solved by using up to 50% (w/w) N-methylmorpholine oxide as an ink additive.⁸³

Again chlorination of wool is the favoured method to pre-treat the fabric to render it readily printable to give strong vibrant prints, which fix well following steaming – the environmental downside of chlorination has been discussed already.

In a study to optimise reactive dye stability in ink-jet inks, Clark *et al.*⁸⁴ found that modification of 2,4-difluoro-5-chloro-pyrimidine dyes by reaction with phenol-*p*-sulphonate produced a reactive dye which was stable in the ink for prolonged periods, even up to a year – the unmodified dye showed significant hydrolysis after only a few weeks' storage. Furthermore, the above authors demonstrated that dye fixation could be achieved by simply batching the print, which had been produced on bisulphite activated wool fabric,⁸⁵ against a moist cotton, interleaving fabric, for 4 h at 25°C. In this manner ink-jet printing could be carried out without expensive steaming equipment to fix the dyes – a system perfect for wool printing with its low production runs to a particular design. This work illustrates the substantial scope for fabric preparation and ink R&D to allow wool fabrics to take part in the digital printing revolution. Investment in this activity is vital.

Since machinery costs are so low digital printers do not have to produce at the same volume as rotary screen printers; in fact a production speed of 20 m per hour would make the machines, when networked like looms, competitive on lots of any size.

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A. K. ROY CHOUDHURY, Government College of Engineering and
Textile Technology, Serampore, India

Abstract: The chapter discusses coloration methods of various synthetic fibres, namely acetate, polyester, nylon, acrylic, polyolefins and elastomeric fibres. These thermoplastic fibres cannot be dyed at ambient temperatures. Dyeing is carried out at a temperature higher than their respective glass transition temperatures. Dyeing may be carried out by exhaust (batch) method or continuous method using dry-heat. The dyes mostly used for dyeing these fibres are disperse, acid and basic dyes.

Key words: dyeing of synthetic fibres, mass coloration, disperse dyes, basic dyes, carrier dyeing, thermosol dyeing.

2.1 Introduction

Hydrophilic natural fibres, namely cotton, wool, silk, etc., are dyed using water-soluble dyes such as direct, reactive, acid, basic, azoic, vat and sulphur dyes. When the hydrophobic synthetic fibres were introduced on the market, they presented a serious problem in that they could not be dyed with the available water-soluble dyestuffs. The search for a new dye class then began which resulted in the development of the 'disperse' dye class. Among the synthetic fibres, the major area of interest is the coloration of polyester fibres (PES), although cellulose acetate, nylon, acrylic and polyolefin fibres are also coloured in considerable quantities.

Aliphatic polyamides, generally referred to as nylons (mostly nylon 6 and nylon 6,6), were the first truly synthetic fibres introduced to the market in the 1940s primarily as replacements for silk filaments. Polyamides contain primary amino end-groups that confer substantivity for acid dyes. The greatest problem in dyeing nylon with acid dyes was the variation in substantivity in different batches due to irregularities in chemical and physical properties of the fibres. Disperse dyes are unaffected by chemical variations of nylon and, therefore, yield more uniform dyeing. However, the use of disperse dyes on nylon is restricted to pale shades because of poor colour build-up and poor wet-fastness properties. Over the course of time, there was great improvement in the regularity of polyamide fibres, with the result that acid dyes could be used on nylons with great success.

Polyester is the leading man-made fibre in production volume and owes its popularity to its versatility alone or as a blended fibre in textile materials. Polyester is highly crystalline and markedly hydrophobic. It is not, therefore, easily penetrable by dyes with large molecules. It also has no chemically active groups and cannot combine with dye anions or cations. Although polyester can be dyed with a few azoic combinations, in practical terms the only dyes which can be used with success are the disperse dyes. Their exhaustion at equilibrium is good, but the diffusion into the fibre is extremely slow. The increased demand for polyester fibres has revived the preparation of new disperse dyes to meet the special requirements associated with the fibre. As polyester is much more thermal-stable compared to other synthetic fibres, it is possible to carry out dyeing at high temperature (130°C) and at high pressure when good colour build-up is obtained with most of the disperse dyes. The dyeing with selected disperse dyes may also be carried out at boil under atmospheric pressure, but the process can be carried out only in the presence of an auxiliary called 'carrier'.

Acrylic fibres have now found a wide spectrum of use where soft, wool-like characteristics are desired. Polyacrylonitriles can be dyed with disperse dyes at boil, but the exhaustion and colour build-up are poor. Better exhaustion can be achieved at high temperature. However, when acrylic fibres are subjected to aqueous treatment above 110°C, excessive shrinkage occurs. To improve the dyeability of acrylic fibres, copolymers called modacrylics are developed, which contain anionic sites to attract basic or cationic dyes. Presently, acrylic fibres are mostly dyed with these dyes at temperatures a little above boil (105–110°C).

Disperse dyes may, therefore, be applied to most of the synthetic fibres, namely acetate, triacetate, acrylic, aramid, modacrylic, nylon, olefin, Saran (vinyl) and polyester. However, for polyester and acetate fibres, disperse dyes are really the only practical means of coloration.

All of these fibres are thermoplastic, i.e. the fibres soften instead of decomposing or igniting when exposed to sufficient heat. Unless the materials are heat-set, they shrink and creases are formed during hot aqueous treatments such as dyeing. In order to make the material dimensionally stable, heat-setting may be carried out in a medium of hot air, steam or hot water. The materials are also to be scoured and bleached, wherever necessary.

2.2 Mass coloration

The difficulties of dyeing synthetic fibres forced colourists to search for alternate methods of coloration. One such method is mass coloration, mass pigmentation or dope dyeing (Ackroyd, 1974; Jordan, 1969), sometimes also known as solution-dyed or spun-dyed. The method is applicable for all man-made fibres – regenerated (e.g. viscose) and synthetic. In this process,

insoluble pigments (including vat pigments) and selected dyes are incorporated in the solution or melt of polymer before it is spun into filament.

Mass coloration is most popular for polypropylene (PP) – the fibre is almost completely (100%) coloured by this process. For polyester, the proportion of mass-dyed fibre increased from 2% in the early 1980s to 5% today and is still growing. Mass-dyed polyamide is estimated to be around 5–10%. Pigmented acrylic is used in Europe and the USA for outdoor application and represents about 3% of the total fibre produced (McKay, 1994).

The advantages of mass coloration are:

1. Economical when a manageable (limited) range of shades is coloured in larger quantities.
2. Absolute shade uniformity, even over very long runs.
3. Excellent all-round colour fastness.
4. During dyeing for a prolonged period, especially at high temperature, undesirable changes may occur in delicate man-made fibres. Mass coloration is simultaneous with fibre production; hence fibre properties are not hampered as long as colorants of specified particle sizes and qualities are used.
5. Cost of coloration is low as no additional dyeing machine is required.
6. In dyeing, a significant quantity of colorant is wasted as unexhausted and unfixed colorant whereas in mass coloration, the wastage of colorant is negligible.
7. Considerable economy in production time, water, energy and chemicals – their supply and disposal.

The disadvantages of mass coloration are:

1. There can be no speedy adaptation to quick-changing fashion trends, especially when demands are varied and spread over small lots.
2. The flexibility in fibre production is minimised.
3. Continuous man-made fibre production sequences are frequently interrupted for change of colour and for cleaning of the equipment from residual colour.

The fibril diameter of man-made fibres used in textile applications is within the range 16–25 μm , depending on fibre fineness (denier) and specific gravity of polymer. The incorporation of coarse pigment particles not only impairs tensile strength, but also jeopardises subsequent processing as a whole. Hence, it is important that the average pigment particle size should be less than 1 μm , although individual particles of up to 2 or 3 μm in size may be tolerated. Pigments, which normally occur in coarse crystalline forms, are subjected to a special grinding process in the presence

of a dispersing system. The stabilised formulation may be either solid or liquid.

For an optimum dispersion to be achieved, the number of aggregates and agglomerates has to be reduced as much as possible. The tendency of pigment crystals to form aggregates is influenced by the particle size distribution, shape, surface treatment, crystalline structure and chemical composition of primary crystals. Aggregation of pigment crystals during processing leads to technological limitations in application, i.e. loss of mechanical strength in mouldings, breakage during spinning, difficulty in consistent colour matching in production and poor optical features of the final product. To achieve an adequate level of dispersion, the pigment is initially dispersed into the polymeric medium. The coloured pre-dispersion is then supplied to the fibre manufacturer. The most common type of pre-dispersion is the master-batched pigments. Here, the pigment is pre-dispersed at a concentration as high as 50% or more in a polymer, and processed into a granular form. The granules of master batches are mixed with uncoloured polymer granules to achieve the desired depth of shade in the fibre after processing (Ahmed *et al.*, 2006).

Various methods of mass coloration are:

1. Single-bath system
2. Master-batch system
3. Direct injection system.

Mass coloration was initially practised using a single-bath discontinuous system in which the pigment dispersion was incorporated into a large quantity of fibre solution or melt in a large mixing tank followed by sending the mixture for spinning. In this method, a large section of the plant is to be washed during change of colour.

In the continuous master-batch system, a quantity of fibre solution/melt is mixed with the pigment paste to prepare a concentrate, which is injected into a blender fed with metered uncoloured fibre solution/melt from the main supply. The blender is located near the spinning head to facilitate cleaning. Subsequently, highly efficient homogeniser and devices have been developed to reduce the human element in the laborious repeated preparation of master batches.

The next development was elegant automatic control systems or direct injection systems giving constant pigment: fibre mixtures irrespective of the fluctuating demands at the spinning machine. Introduction of high efficiency mixer together with precision piston and flexible diaphragm pumps capable of metering diluted pigment dispersion of water-like viscosity accurately against the high-pressure flow of fibre solution enabled the master batches

to be dispensed with altogether. This direct injection system is widely popular now.

2.2.1 Mass coloration of acetate

Both single-batch and master-batch methods are used. Direct injection system may be practised with solvent-soluble dyes, but the problems arise from limited solubility of dyes and control of volatile solvents.

Two broad classes of colorants are used for cellulose acetate – pigment and solvent-soluble dyes. The chemical types of pigments suitable for acetate are more than those of viscose as the pigments do not have to withstand strong alkali and acid, but all must be insoluble in acetone.

Some of the colorants suitable for mass coloration of cellulose acetate fibres are:

- C.I. Pigment Yellows 3 and 17
- C.I. Pigment Reds 2, 7 and 144
- C.I. Pigment Blues 15 and 60
- C.I. Pigment Brown 22
- C.I. Pigment Green 7
- C.I. Pigment Black 7
- C.I. Vat Yellow 4
- C.I. Vat Oranges 3 and 7
- C.I. Vat Blue 1.

Most of the solvent-soluble dyes mentioned in the colour index can be used for mass coloration of acetate fibres and they give lustrous transparent colours. Nevertheless, fastness with all such dyes may not match with that obtained with pigments. Chemical types include monoazo, metal-complex azo, anthraquinone and phthalocyanine compounds – anionic, cationic or non-ionic. They are commercially pure dyes, free from standardising and dispersing agents. The criterion for selection is the solubility of the dye in the dope at spinning concentration.

2.2.2 Mass coloration of acrylics

The lack of suitable dyes and dyeing processes for acrylics created a spur to mass coloration. The spinning of acrylic polymer may be carried out in four ways:

1. Dry spinning from dimethylformamide (DMF) solution
2. Wet spinning from DMF solution

3. Dry spinning from dimethylacetamide (DMA) solution
4. Wet spinning from sodium thiocyanate solution.

Clearly, dyes soluble in the above solvents cannot be used in wet-spun processes. Even such dyes can cause severe spinneret encrustation due to the high temperature of the spinning solution (150°C) and high extrusion temperature (400°C). High-grade pigments like the quiniacridone and perylene types are particularly valuable because of their high solvent resistance.

The acrylic filament, wet spun from sodium thiocyanate solution and destined for staple fibre, may be dyed in tow form. The filaments after extrusion are washed in tow form and then dyed by a continuous process with modified basic dyes having the required solubility and stability at low pH and at low concentration of sodium thiocyanate.

2.2.3 Mass coloration of nylon

Compared with other thermoplastic fibres, polyamide fibres offer a much lower choice of colorants, because they must be stable at high melting temperature and reducing nature of nylon melt. The mass coloration of nylon is restricted to filament only. Nylon can be mass coloured in three ways:

1. Autoclave coloration, i.e. addition of colorants before polymerisation. The method has not survived because of the combined effects of the strongly reducing character and temperature of nylon melt (250°C for nylon 6,6 and 215°C for nylon 6). In addition, hot monomer may cause flocculation of pigment slurries. Colorants initially used were mostly inorganic cadmium pigments, oxides of iron and chromium, carbon black, etc. Numerous heat-stable organic pigments, namely phthalocyanine, anthraquinone and quinacrydone derivatives, have also been suggested. The incorporation of colorants in the autoclave has declined considerably. The process of changing of colour is inconvenient and cost of cleaning is high. Moreover, there are chances of degradation of the polymer and subsequent undesirable effects on yarn quality.
2. 'Chip coating', i.e. addition of colorants after polymerisation and before spinning. The method is comparatively better as the time of contact, between colorants and molten polymer, is less and autoclave contamination is eliminated.

In chip coating, colorants in one form or other are applied to the surface of the chips. If the coating is consistent and stable, the technique leads to uniform distribution of colorant in the polymer and special a mixing procedure is not necessary. The colorant should be an integral

constituent of the extender (colorant vehicle). The use of water-miscible liquid aliphatic acids, hot water-soluble alcohols, high temperature grinding and plastic-milling with formic acid are suggested.

The chip coating process is more flexible than autoclave coloration and it results in improved fibre quality. On the other hand, disadvantages of chip coating include colour variation due to dusting off and large amounts of costly extenders are required.

An approach to solving these problems is 'chip dyeing', i.e. dyeing of nylon chips before spinning into fibres in an aqueous dyebath using processes and equipment somewhat similar to those used for dyeing of nylon textiles. The method is frequently used for nylon 6 and to a less extent for nylon 6,6. The dyeing may be simultaneous with aqueous monomer extraction process, an essential step for nylon 6 (not for nylon 6,6). The dyes should have necessary heat stability. Numerous metal-complex azo and anthraquinone dyes are suitable for the purpose. The dyes should have sufficient absorption power, which is also influenced by chip size and liquor ratio. No dyeing auxiliary is necessary. The pH is set below 7.0 using ammonium acetate, acetic acid or formic acid. A dyeing time of 1–5 h may be necessary. Dyeing in autoclave at 120–130°C improves bath exhaustion and shortens dyeing time.

The environment-compatibility expected from dope dyeing is not assured in the chip dyeing process, owing to the formation of large volumes of wastewater. Intermediate storage of large quantities of polymer in several shades may be unavoidable.

3. Mixing of colorants with polymer just before spinning, either by batch-wise admixing (directly or master-batch system), continuous admixing in a mixer before spinning or injecting melts of master batch, and spinning polymer into the discharge zone of the main extruder with a mixing pump.

2.2.4 Mass coloration of polyester

Mass-coloured polyester fibres are available in both staple and continuous filament forms, the staple fibre form being more important. Though the temperature of polyester melt is high (260°C), it does not have reducing nature.

Autoclave coloration or chip coating may be done with pigment dispersion, but chip dyeing is not popular. This is because polyester is dyed either with carriers at boil or at high temperature. In the first case there is a chance of contamination of the polymer-melt, while in the second case, polymer hydrolysis is liable to occur.

The range of pigment colorants suitable for polyester roughly matches that for nylon. The use of dyes is not excluded, but it seems likely that

polymer-soluble dyes will be preferred for both nylon and polyester. For nylon, anthraquinone derivatives and chrome-complex dyes, and for polyester, azo, anthraquinone and azopyridones are suitable.

2.2.5 Mass coloration of polyolefins

Despite desirable properties, PP fibres traditionally have suffered from a major drawback that has limited their adoption in textile apparel applications – in contrast to other fibres, conventional PP fibres cannot be dyed. Instead, the colour has to be imparted at the fibre extrusion step through mass coloration or solution dyeing. The process involves adding a relatively thermally stable pigment colorant during the melt spinning of the fibre. The pigments used are not usually miscible with PP. Thus, the pigments are present as discrete particles in the fibre, and the colour imparted becomes permanent in the fibre.

Because of lower melt temperature (165°C), a wider range of pigments including chrome pigments, inexpensive azo pigments and toners are used. However, fine PP filaments are extruded at temperature as high as 300°C and high thermal-stable pigments, similar to those used for nylon and polyester, are to be selected for that purpose.

Currently, some of the most widely used pigments for the mass coloration of PP include C.I. Pigment Red 57:1, C.I. Pigment Blue 15:3, C.I. Pigment Yellow 62, C.I. Pigment Green 7 and C.I. Pigment Red 48:2 (Lewis, 1988).

2.3 Disperse dyes

The Society of Dyers and Colourists (UK) defines disperse dye as ‘a substantially water-insoluble dye having substantivity for one or more hydrophobic fibres, e.g. cellulose acetate or polyester and usually applied from fine aqueous dispersion’.

While dyeing from aqueous media the bulk of the dye is in suspension, but at least during the initial stage of dyeing, *transfer* of dye into the fibre takes place from a very dilute aqueous solution of the dye. Such pockets containing dissolved dyes are continuously replenished by progressive dissolution of particles in suspension.

Due to their non-ionic nature, disperse dyes are volatile and the dye-vapour is strongly adsorbed by hydrophobic fibres. This is the basis for thermosol dyeing (heat-fixation) and heat-transfer printing processes.

Disperse dyes are mainly used for acetate and polyester fibres. The dyes for secondary cellulose acetate are well established. For highly hydrophobic triacetate fibre, the molecular size of the dye is the limiting factor. Polyester fibres are generally dyed at high temperature. The dyed and printed polyester materials are often subjected to heat treatment. Hence, dyes of greater

molecular size having good sublimation and light-fastness and providing good colour yield on polyester are desirable.

On nylon, disperse dyes can cover barré effect (structural differences) resulting from variation in end amino groups. However, due to limited fastness properties, dyeing is restricted to pale and medium shades on nylon hosiery and carpets.

On acrylic fibres, light-fastness of disperse dyes is good, but limited colour build-up restricts dyeing to pale shades only.

Some characteristics of disperse dyes are:

- (a) Low-molecular-weight substances, mostly derived from azo, anthraquinone and diphenylamine.
- (b) Crystalline materials of high melting point ($>150^{\circ}\text{C}$). They are milled with dispersing agents to produce stable dispersions in dyebath, $0.5\text{--}2\text{ }\mu$ in particle size. As they are applied in the form of very fine aqueous dispersions, both particle size and dispersion stability are extremely important. Ideally, disperse dyes should disperse extremely rapidly when added to water and give a stable dispersion of very fine and uniform particle size. The dispersion should be stable during dyeing in the presence of auxiliaries, including carriers and levelling agents. Some aggregation of dye may precipitate on the fibre surface in the presence of surface-active agents and at temperature higher than 100°C , which are to be removed after dyeing by reduction clearing.
- (c) Available in both powder and liquid forms. The powder brand contains considerable amount of dispersing agent (e.g. a naphthalene sulphonic acid-formaldehyde condensate) and possibly a wetting agent. The liquid dyes are concentrated and free-flowing aqueous dispersions. The advantages claimed for the liquid brand are freedom from dusting, easy preparation of dyebath and padding liquor and suitability for automatic metering systems called 'auto-dispersing'. They contain lower amounts of dispersing agents and give higher colour yield and brighter dyeing in pad-thermosol process.
- (d) Non-ionic in nature devoid of strong solubilising groups like sulphonic or carboxyl groups, although weak solubilising groups like aromatic or aliphatic $-\text{NH}_2$, $-\text{NHR}$ and $-\text{OH}$ groups may be present.
- (e) Relatively low solubility (at least 0.1 mg/L) in aqueous medium under dyeing conditions. Aqueous solubility at 80°C ranges from 0.2 to 100 mg/L . As solubility increases logarithmically with temperature, a considerable amount of dye may be in solution at 130°C . On cooling, the dye may crystallise as large particles.
- (f) The saturation level of pure disperse dyes in the fibre is relatively high ($30\text{--}200\text{ mg/g}$ of fibre).
- (g) Due to the absence of ionisable groups, disperse dyes have the tendency to sublime without decomposition. Consequently, colour of disperse-dyed fabric may fade while ironing.

- (h) The colour yield, brightness and shade of disperse dyes remain unaffected in the presence of hard water up to 50° Clark (British) hardness.
- (i) With other dyestuff classes, identity of chemical structure establishes all dyeing and fastness properties. But this is not true with disperse dyes. The disperse dyes having identical chromophore (indicated by C.I. number) produced by different manufacturers may not give same shades on dyeing. The shade produced depends on several factors such as shape, size and volume of the dye crystals, coloured impurities or isomers, type and amount of dispersing agents and products added for standardisation.
- (j) Disperse dyes show thermal migration, i.e. migration of dye from core to surface while drying of dyed goods at 170°C or above. Migration is more common in case of disperse dyes of high-molecular weight having high sublimation fastness. Whenever thermal migration poses a problem of low wash-fastness, the remedy is to post-scour the dyed material followed by drying at 140°C or below. Some processing aids (e.g. spinning or knitting oils) and finishing agents may also cause thermal migration of disperse dyes.

The commercial names of some disperse dye ranges are Dispersol (BASF, Atic), Cibaset (CIBA), Foron (Clariant), Resolin (Dystar), etc.

2.3.1 Classification

BASF characterise their Palanil disperse dyes by 'diffusion number', which is based on the degree of penetration of the dye into polyester film under defined dyeing conditions. The diffusion number is important for assessing some important properties of disperse dyes, notably their combinability and suitability for a particular application. The larger the molecular size of the dye, the slower the rate of diffusion and higher the energy required for its application. The dry-heat or sublimation fastness for such dye will also be higher. Therefore, disperse dyes may be classified into three categories – low, medium and high-energy dyes.

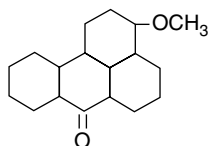
The Committee on the Dyeing Properties of Disperse Dyes of the Society of Dyers and Colourists (UK) formulated a test for classifying disperse dyes on cellulose acetate on an A–E scale (SDC, 1964). Class-A dyes have the best migration properties, the widest range of application temperature, best colour build-up and fastest dyeing rate. Class-E is the worst in terms of the above properties and the dyeing rate is slowest. The work was subsequently extended to cover triacetate and nylon.

On the basis of exhaust dyeing of polyester at high temperature (130°C), the results of four tests were published in 1977 (SDC, 1977) covering critical dyeing temperature, migration, build-up and diffusion rate. Control dyes are specified for use in each test and the behaviour of the dye under test is expressed on either an A–D or A–E scale, where A represents the most

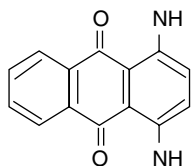
satisfactory in relation to the above properties and D or E represents the least satisfactory for the respective scale.

The properties of various classes of disperse dyes are listed below:

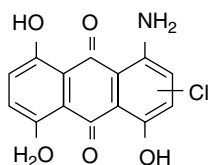
1. Dyes with no suffix, e.g. C.I. Disperse Yellow 13 (Fig. 2.1), are suitable for acetates and nylon.
2. Class-A dyes, e.g. C.I. Disperse Violet 1 (Fig. 2.2), are suitable for acetates and nylon. They are of some use for polyester, but fastness to heat treatment is low.
3. Class-B dyes, e.g. C.I. Disperse Blue 56 (Fig. 2.3), show excellent dyeing behaviour on polyester fibres. They provide good coverage of physically variations as in textured yarn. Heat-fastness of dyed material is moderate. Selected dyes are suitable for acetates and nylon.
4. Class-C dyes, e.g. C.I. Disperse Orange 30 (Fig. 2.4, Example no. 3, section 2.3.2), in general are suitable for acetate and triacetate. They are all-round suitable for dyeing polyester by carrier method, high-temperature method and dry-heat-fixation method, giving better heat-fastness than Class-B dyes.
5. Class-D dyes, e.g. C.I. Disperse Blue 183 (Fig. 2.4, Example no. 4, section 2.3.2), are intended for polyester dyeing of maximum fastness to heat treatment including resin finishing. Application is recommended by



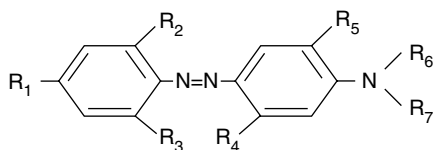
2.1 C.I. Disperse Yellow 13.



2.2 C.I. Disperse Violet 1.



2.3 C.I. Disperse Blue 56.



2.4 Aminoazobenzene.

high-temperature method and dry-heat-fixation method. However, they are unsuitable for carrier method. Selected dyes are suitable for nylon dyeing of high wet-fastness.

ICI disperse dyes (Dispersol) were classified into B, C and D classes (dyes without suffix and suffix 'A' are obsolete), whereas Clariant disperse dyes have been classified into S (low energy), SE (medium energy) and E (high energy) classes.

In order to save time, dyeing should be started at the highest possible temperature and the rate of temperature rise should be the highest possible without hampering levelness. The critical temperature test has been developed in which visual estimations are made of the temperature at which 50% exhaustion of specified amount of dye is obtained within 20 min. In fact, two tests are carried out at light and medium depths using one-fifth and twice the amount of dye needed to produce ISO 1/1 standard depth.

The dyeing is carried out for 20 min at five temperatures, namely 85, 90, 95, 100 and 130°C. The temperature at which colour yield is half of the exhaustion at 130°C is defined as the 'critical temperature' for the particular dye. The average rate of exhaustion at the critical temperature is about 2.5%/min. In older types of jet machine with slower rates of flow (1.5–2.0 cycles/min), the starting dyeing temperature should be below critical temperature to avoid unlevelness. In modern rapid jet dyeing machines, the rate of flow is rapid and dyeing can be started at the critical temperature. Disperse dyes may be rated as A, B, C and D according to critical temperature of the disperse dyes (≤ 85 , 90, 95 and $\geq 100^\circ\text{C}$, respectively).

According to Clariant, the critical temperature zone for high-temperature dyeing is the temperature zone in which the last 80% of the dye is exhausted into polyester fibre. Level dyeing can be obtained if the heating rate is controlled through this temperature zone. Depending on the dye type and amount applied, the critical temperature zone also depends on the chemical system in the dyebath and the polyester substrate. For dyeing with combination of disperse dyes, the lowest and the highest critical temperatures of the disperse dyes in the combination dictate the limits of the critical temperature zone. The critical temperature zone for three Foron Dyes (Clariant) belonging to three energy classes are shown in Table 2.1.

Table 2.1 Critical temperature zones of three Foron (Clariant) Disperse Dyes at low and high depths

Dye	Depth	Zone	Depth	Zone
Yellow S6GLI	0.13	100–121	0.8	111–130
Red SE4BLI	0.17	108–124	1.0	114–134
Navy S-2GRLI	0.54	102–120	4.8	115–136

Note: *Depths* are in % and represent 1/3 and 2/1 standard depth (light and deep shades, respectively), *Zones* represent temperature ranges in °C.

Table 2.2 Comparison of various parameters of conventional and rapid jet dyeing machines

Parameter		Conventional	Rapid
Heating rate (°C/min)	Maximum	2	6
	Usual	1–1.5	2–5
Liquor interchange (cycles/min)		2	6
Rate of liquor flow (L/min/kg)		25–30	60–80
Cooling rate (°C/min)		2	5
Dyeing cycle (h)		2.5–3	1–1.5
M:L ratio		1:10–15	1:6–8
Flow capacity (L/min)		2500	8000

In conventional jet dyeing machines, the maximum heating rate is 2°C/min, whereas in rapid jet dyeing, the heating rate normally is 6°C/min and in advanced machines like Hisaka and Calibaut-de-Bliqy jet dyeing machines, 8–10°C/min. The various parameters in conventional and rapid-dyeing machines are shown in Table 2.2.

Below critical temperature, the temperature can be increased at a higher rate. In rapid jet, the rate may be 6°C/min followed by about 2°C/min in the critical temperature zone. In conventional machines, the maximum heating rate may be 2°C/min, which is to be further reduced to 1.5°C/min in the critical zone.

To reduce the dyeing time further, quick-fixable rapid dyes may be selected so that satisfactory diffusion and fixation may be achieved within 10–20 min in rapid-dyeing machines as compared to much higher times (even 50 min) by the conventional dyes in conventional jet machines. The total dyeing cycle may be reduced to 50–70 min as compared to 180 min in conventional process.

Clariant has produced rapid dyes: Foron RD range consisting of Foron Yellow RD-4GLS, Red RD-GL, Rubine RD-GFL, Blue RD-GL, Navy RD-2RL and Black RD-RL.

The main characteristics of these rapid dyes are:

- Perfect dispersion stability at all dyeing temperatures up to 140°C.
- Uniform absorption on the fibre.

- (c) High colour build-up, equivalent to 6/1 standard depth.
- (d) Due to high rate of diffusion, fixation time is shorter – 20 min at 130–135°C even for jet-black shade.
- (e) Good combinability and reproducibility.
- (f) Moderate fastness to sublimation, i.e. of the Foron SE-standard.

A typical exhaust dyeing application sequence for polyester can be divided into three phases, namely:

1. The heating or adsorption phase.
2. The high temperature or diffusion phase.
3. The reduction-clearing phase.

In optimising dye selection to maximise ‘Right First Time’ production, it is important to know the behaviour of disperse dyes in each of these three critical phases. In particular, the ‘controlled coloration approach’ demands that a consistent selection of dyes be made in each shade area, which displays good compatibility through the three phases of dyeing.

The compatibility of disperse dyes is unimportant and any combination of dyes can be used, provided sufficient time is given and appropriate auxiliaries are used. The choice of disperse dyes for polyester is not influenced by dye interactions or competition for dye sites, as in the case of acid dyes on nylon. In practice, however, to optimise the productivity of the operation, it is essential to minimise process times. In modern rapid-dyeing for polyester, compatibility of dyes is important, as the process does not necessarily allow for the ‘late’ dye to adsorb or ‘poor’ levelling dye to migrate or the ‘slowest’ dye to diffuse.

If shades are dyed with a range of compatible disperse dyes, with the same combination used in each area of colour space, each such dyeing becomes predictable and consistent. Choice of the dye for matching is then driven by Right-First-Time through the use of guidelines of selection with a colour map, as illustrated for the compact Dispersol C-VS dyes range from BASF. This approach allows for a build-up of a ‘shade bank’ of production recipes and software such as ‘Smart Match’ (Datacolor) can be utilised to predict new recipes solely based on actual production shades on a particular quality of substrate, rather than requiring laboratory matching.

The ‘compact’ Dispersol C-VS (BASF) dyes are a short range of selected medium- energy dyes, which demonstrate similar application characteristics in rapid-dyeing cycles on polyester. The disperse dyes with similar adsorption characteristics are used for combination shades so that the adsorption behaviour and critical temperature range for control are reasonably consistent and predictable. To minimise time at high temperature, dyes with relatively rapid diffusion rates should be employed.

Achievement of Right-First-Time also depends on meeting the customer's fastness specification, so that the selection of dyes and choice of treatment in the reduction-clearing phase is appropriate. A key criterion in the selection of dyes for the compact Dispersol C-VS series is their ease of clearing, so that high standard of fastness can be achieved without reduction clearing in the majority of shades (Collishaw *et al.*, 1998).

2.3.2 Chemical structure

The disperse dyes possess any of the following chemical structures:

- (a) Azo
- (b) Nitrodiphenylamine
- (c) Anthraquinone
- (d) Methine
- (e) Heterocyclic rings.

Azo dyes

Azo dyes represent the largest and most important group, and chiefly cover yellow, orange and red hues. The dyes are relatively cheap and generally they do not require numerous intermediate stages during manufacture.

The most important subgroup, aminoazobenzene derivatives (Nunn, 1979), has the chemical structure as shown in Fig. 2.4 where

R_1 = electrophilic group

R_2 and R_3 = H or electrophilic groups

R_4 and R_5 = H or nucleophilic groups

R_6 and R_7 = H or alkyl or substituted alkyl groups.

Examples are:

1. C.I. Disperse Orange 5, where $R_1 = \text{NO}_2$, $R_2, R_3 = \text{Cl}$, $R_4, R_5 = \text{H}$, $R_6 = \text{CH}_3$, $R_7 = \text{CH}_2\text{CH}_2\text{OH}$ (class-A dye, suitable for secondary acetate).
2. C.I. Disperse Red 19, where $R_1 = \text{NH}_2$, $R_2, R_3, R_4, R_5 = \text{H}$, $R_6, R_7 = \text{C}_2\text{H}_4\text{OH}$ (class-B dye, suitable for secondary acetate, dull scarlet on nylon).
3. C.I. Disperse Orange 30, where $R_1 = \text{NO}_2$, $R_2, R_3 = \text{Cl}$, $R_4, R_5 = \text{H}$, $R_6 = \text{C}_2\text{H}_4\text{CN}$, $R_7 = \text{C}_2\text{H}_4\text{OCOMe}$ (class-C dye).
4. C.I. Disperse Blue 183, where $R_1 = \text{NO}_2$, $R_2 = \text{CN}$, $R_3 = \text{Br}$, $R_4 = \text{NHCOEt}$, $R_5 = \text{H}$, $R_6, R_7 = \text{Et}$ (class-D dye, suitable for polyester).
5. C.I. Disperse Red 73, where $R_1 = \text{NO}_2$, $R_2 = \text{H}$, $R_3 = \text{CN}$, $R_4, R_5 = \text{H}$, $R_6 = \text{C}_2\text{H}_4\text{CN}$, $R_7 = \text{Et}$.

Blue azo disperse dyes, based on benzenoid diazo components, have continued to enter into the areas formerly dominated by anthraquinone dyes and it is now possible to cover the range from bright royal blue to greenish blue with good, all-round fastness properties. Such dyes derived from Fig. 2.4 are as follows:

1. $R_1, R_2 = \text{NO}_2, R_3 = \text{Br}, R_4 = \text{NHAc}, R_5 = \text{OEt}, R_6, R_7 = \text{C}_2\text{H}_4\text{OAc}.$
2. $R_1 = \text{NO}_2, R_2, R_3 = \text{CN}, R_4 = \text{NHAc}, R_5 = \text{H}, R_6, R_7 = \text{Et}.$
3. $R_1, R_2 = \text{NO}_2, R_3 = \text{CN}, R_4 = \text{NHAc}, R_5 = \text{H}, R_6 = \text{Et}, R_7 = \text{CH}_2\text{C}_6\text{H}_5.$

Diazo dyes have attracted increasing attention with the advent of polyester fibres where they give satisfactory properties at a reasonable price. However, the use of relatively cheap intermediates is counterbalanced to some extent by the need to carry out diazotisation and coupling, twice each. They are particularly important for yellow and orange colour dyes such as C.I. Disperse Orange 13 and Orange 29.

Azo disperse dyes are largely unaffected by burnt gas fumes. However, azo blues are much duller and less light-fast than anthraquinone blues.

Nitrodiphenylamine dyes

Nitrodiphenylamine dyes continue to be a relatively small class of dyes covering mainly yellow and orange-yellow hues. They are still used on account of their low cost, ease of manufacture, very good fastness to light in pale colours and their usefulness in producing greens with blue anthraquinone dyes whilst maintaining good fastness to light. By increasing molecular size or by introducing polar groups, sublimation fastness can be improved. Probably the best known commercial dye of this type is C.I. Disperse Yellow 42, a Class-C dye. The colour strength of the dye may be increased by the addition of an azo chromophore.

Anthraquinone dyes

Anthraquinone dyes are a large and important group covering the hue range from greenish yellow to bluish green. However, these dyes are particularly valued for the production of bluish red, violet, blue and bluish green dyeing. The simple anthraquinone dyes are bright and stable under dyeing conditions. Dyes of this class will probably not increase their market share in the near future because:

1. They are somewhat weaker in tinctorial value than many azo dyes.
2. Several intermediate production stages increase capital investment with consequent increase in dye cost.
3. Many dye intermediates required for their production are derived from anthraquinone- α -sulphonic acid, which requires a mercury catalyst. This may create pollution problems and alternative methods are to be established.

Examples are C.I. Disperse Violet 1 (Fig. 2.2) and C.I. Disperse Blue 56 (Fig. 2.3). A few other anthraquinone disperse dyes are:

1. C.I. Disperse Yellow 77
2. C.I. Disperse Oranges 5, 6
3. C.I. Disperse Red 86
4. C.I. Disperse Blue 73.

Anthraquinone dyes containing primary or secondary amino groups are susceptible to fading by burnt gas fumes, e.g. when 1, 4, 6, 8 tetra-aminoanthraquinone dye is used for dyeing and printing on secondary acetate and triacetate. Introduction of electronegative groups (e.g. -OH) ortho to the amino groups, arylation of the amino groups (as in the case of C.I. Disperse Blue 27), and/or omission of amino groups altogether, increases resistance to burnt gas fumes. The sublimation fastness of the dye is also improved due to the hydroxyethyl group attached to the pendant phenyl ring in the above dye. Similarly, C.I. Disperse Blue 73 has very good fastness to light and adequate sublimation fastness to most of the end-use. However, if the molecule becomes weakly acidic, it becomes unstable to alkali with consequent deterioration in dyeing properties.

Quinizarin is a traditional and readily available anthraquinone intermediate, which condenses readily with arylamines particularly in the presence of a proportion of leuco-quinizarin to produce violet to green dyes for polyester, e.g. C.I. Disperse Violet 27.

Methine (styryl) dyes

Methine (styryl) dyes are a small group that was originally introduced to produce greenish yellow dyes for secondary acetate. The early dyes of this type were somewhat lacking in sublimation fastness and rather unstable when applied at high temperature, especially under alkaline conditions. However, improvements were made by increasing the molecular size by using groups like 4'-benzyl- β -phenoxyethyl. Dyes having more complex structures are prepared by condensing pyrene, triphenylamine and phenoxazine with reactive methylene compounds like malonitrile. They are all fluorescent greenish yellow dyes with the exception of the latter which is orange.

Heterocyclic dyes

A number of heterocyclic dyes are particularly useful for producing bright colours, especially greenish yellow, although application and fastness properties are not always ideal. For example, C.I. Disperse Yellows 54 and 64 are quinophthalone compounds, but are banned now. Another member

belonging to this group is C.I. Disperse Yellow 206. Although not as green and bright as many of the styryl dyes, they possess good colour build-up and good fastness to light with the advantage of a high degree of stability under most application conditions, like anthraquinone dyes.

Coumarin dyes are useful for the production of fluorescent greenish yellow dyes for polyester.

Thiophene-based azo dyes (Dispersol XF dyes) cause minimum staining on cellulose. A high degree of transfer of dye occurs from cellulose to polyester during thermofixation and the material can be cleared easily in hot alkali without lengthy reduction clearing.

Benzodifuran dyes represent a new class of disperse dye covering mostly red hues. These dyes possess very bright shades and excellent fastness properties. Incorporation of benzodifuran groups has resulted in disperse dyes of virtually zero thermal migration during finishing and the highest levels of wet-fastness. With the increased pressure on domestic washing-fastness requirements, the disperse dyes must withstand the most severe washing detergents.

2.3.3 Dyeing theory

When a low-molecular-weight crystalline solid is heated, there is a change of state at the melting point. The individual molecules separate spontaneously and the solid changes to a free-flowing liquid. Polymer molecules cannot separate so easily because their length inhibits the spontaneous molecular disengagement, which characterises the melting of a simpler solid. Instead, only segments of any polymer molecule can separate as the temperature is raised. The temperature at which the separation begins is well defined and is called 'glass transition temperature' or T_g . When the temperature is exceeded, the frequency of the change in the position of polymer segments, called segmental jumps, increases exponentially with increasing temperature. In fibre, this leads to a rapid increase in the rate of dyeing.

In the presence of certain compounds, the glass transition temperature (T_g) of the polymer lowers. They are referred to as plasticising agents. The most familiar plasticising agent for thermoplastic fibres is water, but generally, plasticising agents are more complicated organic compounds. The semi-empirical WLF equation (Williams *et al.*, 1955) describes the variation of the viscosity of polymer solutions or the viscoelastic properties of solid amorphous polymers with temperature. The free-volume theory derived from the WLF equation proposes that all electrical and mechanical relaxation properties of polymers or viscoelastic properties (like creep, stress relaxation, etc.) are interrelated and are determined by segmental mobility and the free volume (space not occupied by polymer molecules) available for movement of the polymer chains. For amorphous rubber-like polymers

in which only van der Waals forces operate, the viscoelastic properties of polymer will be similar at equal values of $(T - T_g)$. Thus, the speed of diffusion of a dye increases with increase in $(T - T_g)$.

Numerous organic compounds of relatively small molecular size increase the rate of uptake of disperse dyes by thermoplastic fibres. Such compounds are called carriers. The concept that the carriers function by opening fibre structure was first proposed by Schuler in 1957 and is still the best mechanistic explanation of carrier activity. Since free volume is temperature-dependent, one explanation of carrier effects is that they reduce the thermal energy needed to achieve adequate free volume for dyeing. Ingamells (1980) concluded that

- (a) Plasticisation or lowering of T_g of the fibre by the carrier influences diffusion of dyes into the fibre.
- (b) Plasticisation action can lead to other changes in the fibre, which may or may not result in fibre swelling.
- (c) Fibre swelling is not necessarily associated with the enhanced diffusion of dyes into fibres.
- (d) Plasticisation leads to increased accessibility of dye sites in acrylic and basic-dyeable polyester fibres.

The four stages of dyeing with synthetic fibres with disperse dyes are as follows:

- (a) A part of the dye dissolves in the water of the dyebath.
- (b) Molecules of dye are transferred from solution to the surface of the fibre.
- (c) The solution in the dyebath is replenished by the dissolution of more solid dye from the dispersion.
- (d) The adsorbed dye diffuses monomolecularly into the fibre.

The process of transfer of dye from aqueous solution to the fibre is comparable with the extraction of a solute from one solvent by a second immiscible solvent resembling the partition of a solute between two immiscible solvents. The dye, in other words, forms a solid solution in the fibre. Laws of partition are applicable and distribution coefficients are related to the solubility of the dye in the aqueous and fibre phases. The rates of the first and second phases of the process mechanism are governed by the solubility in both phases. The crystal forms are of considerable importance: some forms of crystal promote equilibrium with stronger aqueous solutions.

The aqueous solubility of disperse dyes is quite low, it lies between 0.3 and 200 mg/L at 100°C and between 0.6 and 900 mg/L (majority between 2 and 70 mg/L) at 130°C. The slow dissolving of disperse dyes in water is promoted by the fine dispersion maintained by the dispersing agents.

The dyeing behaviour with disperse dyes of polyester differs from other synthetic fibres like nylon and secondary acetate in the rate of dyeing. Polyester fibres dye very slowly below 100°C. At 85°C, the temperature at which secondary acetate is normally dyed, dyeing rate on polyester is between 700 and 1000 times slower than those on nylon and acetate. However, if sufficient time is allowed for the polyester fibre to come nearly to equilibrium with the dyebath, it can take up approximately the same amount of dye as secondary acetate does, and in most cases about twice as much as nylon.

The coefficient of distribution of the dye between the fibre and solution phase in the bath decreases as the temperature of the bath increases. The apparent higher colour yield at higher dyeing temperature is due to higher rate of dyeing. At 85°C, for example, the process of building up a medium depth of dyeing on polyester may require several days. The rate of dyeing of polyester materials continues to increase as the processing temperature is raised, so that at temperatures in the neighbourhood of 200°C, fully penetrated dyeing can be produced in a very short time (1 or 2 min).

There is reason to believe that hydrogen bonding takes place between primary amino groups of dye and acetyl groups of acetate fibres. Van der Waals forces and dipole interactions may contribute to the retention of the dye after it has diffused into the fibre.

2.3.4 Function of dispersing and levelling agents

The main functions of dispersing agents are:

- (a) To assist the reduction of particle size of disperse dyes during finishing.
- (b) To facilitate reverse change from powder to dispersion when the dyebath is prepared.
- (c) To maintain dispersion during dyeing.

Dispersing agents increase the aqueous solubility of disperse dyes. Bird (1954) showed the aqueous solubility of various disperse dyes increases at 25°C in the presence of 1-oleyl-4-anisidine-2-sulphonate and at 80°C in the presence of other dispersing agents. They also affect both the rate and the extent of uptake of disperse dyes on hydrophobic fibres. Bird (1954) and later Thakore, Shah and Mittal (1987) showed that dispersing agents lowered the exhaustion of disperse dyes, the former showed on cellulose diacetate while the latter on polyester at 130°C with increasing concentration of Dispersol F (Sandoz, now Clariant).

Ligninsulphonic acid obtained from Kraft paper process is recommended as dispersing agent. For more hydrophilic disperse dyes, lignin of low

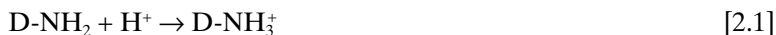
degrees of sulphonation should be used. However, some lignosulphonates are brown in colour and may discolour fibres by absorption. In enclosed vessel, they may also act as reducing agents destroying some azoic disperse dyes. Modern dispersing agents are high-molecular weight compounds and some may be polymeric versions of sodium dinaphthylmethane sulphonate. Anionic dispersing agents may be based on methylated naphthalene sulphonic acid-formaldehyde condensate. Non-ionic dispersing agents are not recommended in dyeing, as they tend to desorb the colour from the dyed fabric. Some of the commercial dispersing agents recommended in dyeing with disperse dyes are Setamol WS (BASF), Lyocol OI (Clariant), etc.

Although dispersing agents are known to improve the migration and levelling of disperse dyes on polyester fibres under high temperature dyeing conditions, levelling during exhaust dyeing is most usually achieved by the addition, to the dyebath, of specific levelling agents, which can be non-ionic or anionic surfactants or their blends. Non-ionic compounds increase solubility of the dye thereby lowering initial strike and overall rate of dye uptake. However, such compounds, whose effects are highly dye-specific, can have a deleterious effect on the stability of dyebath dispersion, especially at a temperature higher than the cloud point of the agent (Burkinshaw, 1995).

2.3.5 Effect of pH

On the basis of the effect of pH on the uptake, azo disperse dyes may be classified into three groups (Shakra *et al.*, 1979):

1. For aminoazobenzene dyes, the dye uptake increases as pH increases due to basicity of the amino groups. In acidic medium the amino group adds a hydrogen proton to form conjugate acid (lyonium ions) as follows:



where D is the chromophore.

With the formation of conjugated acid, the solubility of the dye increases, thereby lowering its affinity for the substrate in acidic medium. In alkaline medium, the solubility of the dye is minimised and its affinity is enhanced.

2. In dyes having hydroxyl groups, the unshared electron pair of the oxygen of the hydroxyl groups may be pulled by nitro or other groups. The hydroxyl group can successfully add hydroxide ions from the solution and forms the conjugate base (lyate ion). The conjugated base is highly dispersed in alkaline medium and has low affinity for the substrate, resulting in lower uptake at higher pH. Again at very low pH, the uptake is lower due to very low dispersibility. Moderate or slightly acidic media

constitute the best environment for dyeing polyester with these dyes. The maximum uptake is achieved at pH 5.0–6.0, when conjugate base cannot be formed and the dye acquires high affinity to the substrate.

3. The third type of disperse dyes are not affected by the pH of the dyeing medium. No advantage is gained by adding acids deliberately to the dye-bath and dyeing is best carried out at pH 5.0–6.0 irrespective of the dye type. It is better to use an ammonium sulphate-formic acid buffer system.

For the dyeing to be level and even, it is essential that the dye dispersion remains stable during the dyeing cycle. A few factors leading to instability of dye dispersion are:

- (a) Unfavourable pH above 6.0.
- (b) Low Material: Liquor (M:L) ratio and high dye concentration.
- (c) Presence of certain electrolytes and levelling agents. For simultaneous use of disperse dyes and reactive dyes on polyester-cellulosic blends, common salt and soda ash are to be added only after disperse dyes have diffused into polyester.
- (d) Fibres of low absorption capacity.
- (e) Liquor turbulence as in jet dyeing.
- (f) A number of disperse dyes have low saturation values; the estimated values for some disperse dyes on staple polyester at high temperature of 130°C are reported to be as follows:
 C.I. Disperse Yellows 42, 126, 229, 236– about 3%
 C.I. Disperse Red 73– about 3%
 C.I. Disperse Red 167– about 4%
 C.I. Disperse Violet 63– about 3%
 C.I. Disperse Blue 183– about 4%
 (All percentages are on the weight of material or o.w.m.)
 It is not feasible to arrive at saturation values in thermosol dyeing.
- (g) Red, purple and blue disperse dyes of anthraquinone group are susceptible to metal ions present in process water and sequestering agents are to be added in the dyebath, if required.

2.3.6 Effect of pre-treatment

Extensive researches have been carried out on modifying polyesters using solvents (Needles and Park, 1996). Researchers (Weigmann *et al.*, 1976) have established that treatment of polyester with suitable solvent results in molecular rearrangement, giving such morphological structure to polyester, so as to make it more dye receptive. A process to produce low-temperature dyeable polyester by methylene chloride pre-treatment has been patented (Ciba-Geigy). Solvent treatments did not have any adverse effect

on the other textile properties of polyester (Murlidharan *et al.*, 2004). The structural modifications of polyester depend upon the extent of interaction between polyester and solvents, associated with their respective solubility parameters (Chidambaram and Venkataraj, 2002).

Chemical modification of polyester, by solvent pre-treatment, results in changes in the dyeability characteristics. When the polyester is pre-treated with a suitable solvent, the internal structure, especially the amorphous region, is changed and thereby more voids, cracks and likes are formed, which facilitate entry of dye molecules into the polymer structure. Also the solvents break the intermolecular bonds and loosen the fibre structure which in turn increases the segmental mobility of the polymer and thus enhances the dye uptake.

Treatment of PES fibre in the mixtures of organic solvents has no influence on the dye diffusion mechanism (the same shape of equilibrium sorption isotherms). Higher uptake is due to the recrystallisation of PES fibre followed by formation of numerous voids and micro-voids which result in a much more open structure (larger number of active centres capable of depositing the disperse dye). Treatment of PES fibre at room temperature in the mixtures of organic solvents leads to the formation of numerous small crystallites (the same as thermal recrystallisation process at 175°C), while treatment at 60°C in the same mixture leads to the formation of small number of larger crystallites that place many fewer restrictions on chain mobility (no change in glass transition temperature) (Mangovska *et al.*, 1995).

2.3.7 Barré

Barré is a dyeing problem due to chemical and/or physical structural differences in thermoplastic fibres. It is defined by the American Association of Textile Chemists and Colorists (AATCC) as 'an unintentional repetitive visual pattern of continuous bars or stripes usually parallel to the weft in the woven fabric or to the course of circular knitted fabrics'.

This may be due to several factors such as differences in thermal history, texturising conditions, yarn tension, denier and origin of the synthetic fibre. The AATCC method of detecting the ability of dye to cover barré is to heat-set three pieces of knitted polyester fabric at 160, 180 and 200°C separately and then to stitch them together followed by dyeing (2% o.w.m.) at pH 5.0 and temperature 130°C. The variations in dye pick-up of the three pieces are compared. The extent of variation may be compared with those of control dyes. C.I. Disperse Blue 56 (low energy) and C.I. Disperse Blue 79 (high energy) suppress and enhance affinity differences, respectively, and accordingly the dye may be classified on a scale of 1–5. Low-energy disperse dyes can cover barré at any depth since they have good migration at 130°C. High-energy disperse dyes have less ability to cover barré, which can be improved by using speciality chemicals like Sandogen PES (Clariant).

These are synergistic mixtures or chemicals having dispersing and migrating action on dyes. By swelling, they aid in the opening up of the fibre structure and improve diffusion of dyes. Sometimes barré can be levelled out by dyeing at higher temperatures of 135–140°C. In case of nylons, barré may be due to variation in amine end-groups or dye sites.

2.4 Disperse dyes on acetate fibres

For dyeing, the liquor is set with 1–2 g/L dispersing agent and the pH is adjusted to 6.5–7.0 for secondary acetate and 4.5–6.5 for triacetate. Sodium dihydrogen phosphate is recommended as the pH controlling agent.

The dye is stirred with 10–20 times (by weight) water at 50–60°C and is allowed to stand for 10 min, with occasional agitation. If the mixture is not sufficiently fluid, more warm water is added. Boiling water should not be used. Pasting should not be done in the presence of highly concentrated surface-active auxiliaries.

The previously dispersed dye is added in the dyebath through a sieve. The material is entered at cold and temperature is raised slowly to 70–85°C and dyeing is continued for 1 h or until the shade is levelled. Disperse dyes differ greatly in the rates of exhaustion and level-dyeing properties. In combination, it is advisable to choose dyes of similar properties. For cellulose triacetate, dyeing is carried out at boil. Higher wet-fastness can be achieved by dyeing triacetate fibres at 130°C and reduction clearing with 2 g/L sodium dithionite, 2 mL/L ammonia and 2 g/L detergent for 30 min at 50°C. A fibre lubricant, often a cationic softening agent, is usually applied in the final rinse after which the material is hydro-extracted and dried.

2.5 Disperse dyes on polyester fibres

The sequence of dyeing polyester is to dye, rinse, reduction clear to remove dye deposited on the surface and finally to soap. Reduction clear may be omitted in case of pale shades. Polyester may be dyed by one of the following three methods:

1. Carrier method
2. High-temperature method
3. Dry-heat or thermosol method.

2.5.1 Carrier method

Poor colour yield of disperse dyes on polyester at boil and the initial lack of pressure-dyeing equipment prompted an early search for carriers, the

products which increase dye uptake by the polyester fibre while dyeing under atmospheric pressure. Numerous water-insoluble organic compounds of relatively low-molecular weight are appreciably absorbed by the polyester fibre and are effective in accelerating dyeing of hydrophobic fibres namely:

- (a) Aromatic hydrocarbons – diphenyl, naphthalene and toluene.
- (b) Phenols – phenol, o- and p-chloro-phenols, o- and p-phenylphenol and m-cresol.
- (c) Chlorinated aromatics – mono, di and trichlorobenzene and chlorinated naphthalene.
- (d) Aromatic acids – benzoic, chlorobenzoic and o-phthalic.
- (e) Aromatic esters – methyl benzoate, butyl benzoate, dimethyl and diethylphthalate, dimethyl terephthalate, phenyl salicylate.
- (f) Aromatic ethers – p-naphthylmethyl ether.
- (g) Miscellaneous – acetophenone, phenyl cellosolve, phenylmethyl carbinol, methyl salicylate and benzanilide.

The ideal carrier for bulk use should:

- (a) produce appreciable colour yield at boil in practicable dyeing time at low carrier cost,
- (b) not affect physical properties of fibre or fastness properties of the dyes significantly,
- (c) not cause carrier spotting and
- (d) be free from toxic or noxious effects during dyeing, in the fibre and in the effluent.

No carrier meets all these requirements and the selection at any time is necessarily a compromise.

In early years of polyester dyeing, the preferred carriers were o-phenylphenol and diphenyl. O-phenylphenol is supplied in the form of water-soluble sodium salt having no carrier action. The free phenol is produced by acidification. In the inverse method, the bath is initially set acidic in which sodium-o-phenylphenol is added in portions when the carrier is gradually released. The bath is acidic throughout dyeing, thereby avoiding decomposition of alkali-sensitive dyes. However, it calls for careful handling of solid carrier. It is therefore supplied as either an emulsifiable liquid, e.g. Optinol B (ICI), or a ready-to-use emulsion, e.g. Matexil CA-OPE or Tumescal OP (ICI). The merits of o-phenylphenol as carrier are:

- (a) Negligible toxicity.
- (b) Applicable up to pH 9.0.
- (c) Suitable for pre-set goods.

The demerits of o-phenylphenol as carrier are:

- (a) Risk of staining.
- (b) Light-fastness of a number of disperse dyes is decreased even after subsequent heat treatment for removal of carriers (Derbyshire, 1974).
- (c) Difficult to remove from fabric.

Diphenyl was used in the early years as a substitute for o-phenylphenol. It is a cream-coloured powder, insoluble in water, but in a readily dispersible state. The merits of diphenyl as carrier are:

- (a) Less effect on light-fastness.
- (b) Application over whole pH range.
- (c) Non-ionic in nature, suitable for dyeing cationic-dyeable polyester with cationic dyes.
- (d) Better levelling of dyes.
- (e) Suitable above 100°C.

The demerits of diphenyl as carrier are:

- (a) Greater volatility of diphenyl causes carrier spotting in open equipment. It is to be added above 80°C. All other carriers may be added at the start, i.e. at 50°C.
- (b) Strong odour. It should be removed by thorough washing because, if left in, it gives a sickly sweet smell to the goods.
- (c) Colour yield is moderate on pre-set goods.
- (d) Tends to crystallise out below 80°C.

Methylnaphthalene is a carrier supplied in the form of self-emulsifiable liquid which may be directly added to the dyebath (23 g/L) at 50–60°C. It gives slightly greater loss of light-fastness, but is easier to remove.

Dichloro- and trichlorobenzene were good carriers. However, they have been banned recently due to their toxicity.

The introduction of carrier dyeing in the early 1950s had an immediate effect on dye selection. All of the A-type disperse dyes recommended for dyeing at boil without carrier had been dropped and the recommended range consisted of B-type dyes with a few C-type dyes. They have, however, lower to medium fastness as compared to D-type dyes, which can only be applied by high-temperature method. Some of the disperse dyes recommended for carrier dyeing are:

- C.I. Disperse Yellows 42, 218, 229 and 236
- C.I. Disperse Oranges 13, 25 and 37

- C.I. Disperse Reds 13, 50, 60, 73, 91, 92 and 343
- C.I. Disperse Violets 26 and 28
- C.I. Disperse Blue 56.

The steps of carrier dyeing are as follows:

1. The dyebath is set at 60°C with 0.5–1 g/L dispersing agent and carrier such as 6.5–9.0 g/L Tumescal OP liq. (45%) (ICI) or equivalent.
2. The pH is set with acetic acid at 5.5–6.0 and the goods are run for 10 min.
3. Required amount of pre-dispersed dye is added slowly and the temperature is raised to boil over 30–45 min.
4. The pH should lie between 5.5 and 6.0 throughout the dyeing process and acetic acid should be added, if necessary.
5. For heavy shades, higher quantity of carrier may be used.
6. Shading dyes, if necessary, should be added after 40 min and a dyeing period of 30 min should be allowed after each addition.
7. After dyeing, the bath should be dropped to a temperature not less than 85°C to prevent deposition of oligomers or low-molecular-weight compounds. The principal oligomer is a cyclic trimer of ethylene terephthalate and small quantities of pentamer, dimer, etc. The quantities of oligomers present in commercial fibres are reported to vary between 1.5% and 3.5%.
8. The material is thoroughly rinsed and reduction cleared with 2 g/L caustic soda (flakes), 2 g/L sodium dithionite and a dispersing agent, e.g. 1 g/L Dispersol VL, Matexil SC-50 (cetyl trimethyl ammonium bromide) or long-chain polyglycol ethers of stearyl alcohol, for 30 min at 70°C. The treatment improves rubbing fastness of disperse-dyed material. Low-pilling polyester and polyester-wool blends are susceptible to caustic alkali and caustic soda may be replaced with ammonia. At the end of the process, the bath should remain alkaline to phenolphthalein and should maintain reducing property, which may be tested with vat-yellow paper.
9. This is followed by soaping with 1 g/L Lissapol D paste and 2 g/L soda ash at 70–80°C for 30 min.

2.5.2 High-temperature method

There are many advantages associated with dyeing polyester at temperatures ranging between 120 and 130°C. The advantages are:

- (a) Heavy shades can be dyed with disperse dyes without a carrier, saving carrier cost and rinsing time for removal of carriers.

- (b) A shorter dyeing cycle is possible under high-temperature conditions using rapid-dyeing machines.
- (c) The deleterious effect of carriers on light-fastness of certain disperse dyes and the obnoxious odour of most carriers, are eliminated.
- (d) A better combination of level-dyeing and fastness properties is obtained by high-temperature dyeing as compared to carrier dyeing at boil.
- (e) Dye selection for high-temperature dyeing is not restricted as in the case of carrier dyeing at boil, and for obtaining adequate colour yields virtually any type of disperse dyes may be used.

For high-temperature dyeing, dye choice can be such as to meet requirements on fastness properties as a first priority, although dyeing properties cannot be altogether neglected for several reasons. The most important is the level-dyeing behaviour in respect of coverage of barré in fabric dyeing or of package-to-package variations in yarn dyeing. The coverage property is better with low-molecular dye, i.e. B-class followed by C-class and poorest with D-class dyes. It is not, therefore, a sound practice to select dyes of the highest fastness properties (D-class) where these are not needed, since the risk of unevenness increases by selection of D-class dyes.

A second factor of importance is the optimum machine utilisation, in view of the high cost of pressurised machines compared with atmospheric machines. Rapid-dyeing machines are developed with this object. Machine utilisation is severely reduced if many shading additions are necessary. The aim is, therefore, to eliminate shading additions altogether by using a sound recipe established by small-scale trial before proceeding to bulk. It is important, wherever possible, to use combinations of dyes whose yield is relatively insensitive to small variations in dyeing conditions. This is best achieved by using dyes that are close to equilibrium at the end of the dyeing sequence. This again argues for the use of rapid diffusing B- or C-class rather than slow diffusing D-class dyes (Derbyshire, 1974).

A very successful development for fabric dyeing was the pressurised beam-dyeing machine. This became the preferred equipment for high-temperature dyeing of flat polyester fabric, the appearance and handle of which is unaffected by the pressure generated on the fabric.

The most important development for high-temperature rope dyeing was undoubtedly the HT jet machine. The first commercial successful example was the Gaston Country Jet, but this was followed by many other designs. The turbulent conditions created by the jet itself automatically ensure that the fabric is moved in its folds so that rope creasing is much reduced.

The general method of dyeing is as follows:

Any alkali used during scouring must be completely removed from the fabric; otherwise degradation of polyester may occur at high temperature.

1. Prepare the dyebath with
 - (a) Dispersing agent – 0.25–2 g/L
 - (b) Sodium acetate-acetic acid (approx. 1 and 0.25 g/L, respectively) or ammonium sulphate (1–2 g/L) – formic acid buffer to set pH at 5.0–6.0.
 - (c) Additionally a levelling agent in case of light shades.
2. The dyeing should be started at 70°C. The temperature is raised slowly to 130°C and maintained for a period of 30–60 min.
3. Shading dyes, if necessary, may be added at 120–130°C, allowing 20 min after each such addition.
4. On completion of dyeing, the bath should be dropped to a temperature not less than 85°C to prevent deposition of oligomers on the surface of the material. The oligomers present in the dye liquor will deposit crystals on any unpolished surface and in regions of high hydrodynamic shear (as in a pump), when the bath is cooled or even without cooling, if crystals are already present. The oligomers deposited on the internal surfaces of dyeing machines are difficult to remove without severe cleaning. It is advisable to clean the machines at regular intervals of 100 h running time. The cleaning process must be more severe than that used for clearing dyed fabrics and a stripping agent like Lyogen DFT (Clariant) (4 g/L) may be added.
5. When heavy shades are dyed, it is advisable to give a reduction-clearing treatment to avoid poor rubbing fastness. This is followed by rinsing and soaping with 1 g/L Lissapol D paste at 70–80°C.

2.5.3 Faults and remedies in exhaust dyeing

Some of the faults commonly occur during exhaust dyeing of polyester with disperse dyes and their remedies are listed below:

- (a) Ending or tailing due to unstable colour dispersion or combination of disperse dyes of different migration properties. The remedy is careful selection of dyes.
- (b) Barré dyeing is mostly due to variation in stretch during texturising. The remedies are the use of low-energy dyes and/or speciality chemicals.
- (c) Skittery dyeing due to inadequate preparation, quality variation of fibre, poor solidity of shade in blends, irregular yarn tension in weaving or knitting. The remedies are proper pre-treatments, careful controls in fabric manufacture and dyeing.
- (d) Localised pale dyeing due to air pockets in the materials. The remedy is the use of suitable non-foaming wetting agents.

- (e) Precipitation of dye when the dyeing depth exceeds saturation value of the dye. The precipitation may be prevented by lowering the depth of dyeing or by using a number of disperse dyes of different chemical structures, but of similar hue.
- (f) Low colour build-up and low brightness due to alkaline process water. An efficient buffer is to be used during dyeing to maintain pH at 4.0–5.0.
- (g) Moiré effect in beam dyeing caused by inadequate heat-setting of polyester and inadequate shrinkage of cellulosic component. Adequate heat-setting is to be done and the fabric may be causticised.
- (h) Poor light-fastness in carrier dyeing due to residual phenolic type carrier. The remedy is to heat-set after dyeing at 170°C.
- (i) Listing due to inconsistent heat-setting, irregular tension in weaving or faulty batching. The remedies are the use of low-energy dyes and proper control in fabric manufacture.
- (j) Centre-selvedge variation because of poor winding, irregular liquor flow, incompatible selection of dyes or poor heat-setting. The remedies are proper control on winding, use of airflow meter and control of width-wise temperature variation in stenter and selection of dyes of similar migration properties (Jaysynth, 1985).

2.5.4 Dry-heat fixation or thermosol method

In the early 1950s, Dupont developed the ‘thermosol method’, a continuous method of dyeing polyester or polyester-blended fabric in which the fabric is padded with aqueous dispersion of dye, dried and baked at 180–220°C for a period of 30–60 s. Because of the hydrophobic characters of fibre and dye and high temperature of treatment, rapid diffusion of dye takes place into the fibre in the absence of carrier or pressurised equipment.

The advantages of thermosol process are (Gibson, 1979):

- (a) As a continuous process, a large yardage can be dyed more economically than by batch processes.
- (b) Excellent utilisation of dye.
- (c) No carrier is required; consequently the chances of spotting and impairment of light-fastness are eliminated.
- (d) The fabric is processed in open width, thereby eliminating the problem of rope marks.
- (e) Dyeability is not affected by previous heat-setting.
- (f) The energy consumption is lower than batch procedures primarily because of shorter dyeing cycles, lower material: liquor ratio and use of energy recovery devices.

The dry-heat method became popular for woven polyester-cotton blends from about 1960s onwards in the USA, the UK and other parts of the world where continuous cotton-piece dyeing was already established. Numerous process sequences are possible, but for polyester component, the most popular sequence for thermosol dyeing is:

Pad with an aqueous dye dispersion → dry → bake → wash off.

The selection of disperse dyes for such blended fabric is complicated. The larger part of disperse dyes after padding and drying resides on the cellulosic component due to its hydrophilic nature. During baking, disperse dyes are transferred from the cellulosic component to the polyester, essentially by vapour transfer rather than contact migration. The final colour yield on the polyester is dependent on the efficiency of transfer, and the fastness properties depend on the residual dye on cellulosic component, which acts as staining, causing poor fastness. Optimum transfer occurs with B-class and C-class dyes, whereas D-class dyes showed low transfer due to poor volatilisation. The disperse dye-stain is largely removed by subsequent reduction clearing. However, where reduction clear is not possible (when reducible cellulosic dyes are present), selection of disperse dyes to minimise staining is important to produce the best fastness.

When impregnated material is dried, the disperse dye particles are in a very fine state of uniform distribution in the capillary network. If this homogeneous distribution is maintained during drying, the efficiency of fixation during subsequent heat treatment would be quite high indeed. This distribution, unfortunately, is not maintained during drying as the dye particles migrate to the surfaces of evaporation where particulate aggregation occurs. Particulate migration in fabric padded with disperse dyes during intermediate drying prior to thermofixation can be a serious problem which may lead to variations of shade and levelness in continuous dyeing operations. Clearly, migration in the warp direction is hardly of much concern. However, migration in the filling direction can occur under conditions of great imbalance in the drying rates. Migration in fabric thickness, i.e. from back to face or from the fabric interior to exterior, will always occur to some extent, even under most properly balanced drying conditions possible in commercial operations. Migration is best minimised by:

- Keeping the pick-up in padding as low as possible.
- Batching the impregnated fabric before drying.
- Drying uniformly without shock.
- Using dyes of low dispersing agent content.
- Employing wetting agent judiciously.
- Including commercial antimigrants in the padding liquor.

The commercial antimigrants, e.g. Amamigrant AM (American Color & Chemical), Primasol AM (BASF), Superclear 100-N (Diamond Shamrock),

etc., are essentially polymeric electrolytes. They bring about a very slight coagulation of the dye particles which reduces the tendency of the dye to move within the fabric capillary network, although the aqueous medium in which the particles originally were dispersed continues to flow to the evaporating surfaces during drying.

With increased use of texturised polyester fabrics, the thermosol method seems to be promising. However, the immediate problems of thermosol dyeing with 100% polyester fabric are migration of dyes on the surface during drying, with consequent poor penetration, inadequate fixation of dye by dry-heat and impairment of bulkiness of the yarn. The combination of efficient migration inhibitor and urea gives good migration prevention and good fixation. Urea is beneficial as fixation accelerator. By use of 100 g/L urea in the pad liquor, good colour yields are obtained with B-class and C-class dyes after baking for 2 min at 170°C. However, the use of urea may cause several problems, such as:

- (a) Inconsistent colour yield and dulling of shades.
- (b) Severe browning and hardening of thickeners.
- (c) Crystallisation of urea on the machines.
- (d) Decomposition of urea forming ammonia which may degrade the dye.

Migration inhibitors are high viscosity acid-stable alginates or polyacrylic acid dispersions sold under the brand names of Sansapol AM (Clariant), Primasol AMK (BASF), Manutex F (Alginate Industries, UK), carboxymethylcellulose, modified guar gum, etc.

At present, various fixation accelerators are available for improving colour yield in high-temperature steaming and dry-heat fixation, which are mostly ethylene oxide condensation products of fatty acids or their amides with ethylene diamine. A few commercial accelerators are Avolan IW, Levalin DHT, Levagal MSF (Bayer, presently DyStar), Noigen EI-40 (Dai-ichi), Matexil PN-HT (ICI), Ekalin FI (Clariant), etc.

Careful dye selection is necessary. High-molecular, high-energy dyes should be of first choice. Medium-energy dyes serve as shading elements.

The steps for thermosol dyeing are as follows:

1. The material is padded cold using 50–60% pick-up with padding liquor consisting of:

Disperse dyes	x parts
Migration inhibitor	5–20 parts or
Sodium alginate	2 parts
Sequestering agent (if necessary)	1 part
Water to make	1000 parts

 Tartaric acid is added to set pH at 5.0 (about 5 g/L).

A small-capacity trough should be used and the dye liquor should be continuously replenished. The padding bowls should have 60–70° shore hardness and ideally the fabric should be padded with vertical nip.

In case of 100% polyester and blended fabrics with pronounced structures where it is difficult to get a level shade, it is advisable to add a leveling agent such as 5–12 mL/L Lyogen DFT (Clariant).

2. After padding, the material is passed through a pre-drying unit, which may be a hot flue chamber, heated can or an infrared pre-dryer.
3. It is then thermofixed at the desirable temperature between 180 and 220°C for 30–60 s. In some countries, pre-heaters are hardly available and instead of a thermosol unit, pin stenters may be used for fixation. Fixation is also possible on the continuous loop steamer where dry hot superheated steam replaces hot dry air; the conditions are 8 min at 180°C for high-energy dyes and 6–7 min at 175–180°C for medium-energy dyes.
4. It is then reduction cleared and soaped as usual.

Optimisation of fixation times may be done by:

 - (a) Accelerating diffusion using highest possible thermosol temperature.
 - (b) Achieving maximum operational reliability with the use of dyes of similar diffusion rate and similar activation energy of diffusion.
 - (c) Using pre-heated fabric – the heating-up time for polyester fabric may be 5–15 s.

2.5.5 Faults and remedies in thermosol dyeing

Some of the faults commonly occur during thermosol dyeing of polyester and their remedies are listed below:

- (a) Listing due to differing nip pressure and migration of colour in intermediate dyeing. The nip pressure should be checked at various points, the wet pick-up should be low and migration inhibitors should be used.
- (b) Two-sidedness may occur due to unequal drying from two sides or due to uneven padding bowl. The temperature and air-current in pre-dryer and the shore hardness of both the bowls should be checked.
- (c) Pale spots or specks may be due to condensation of water or foam. The remedies are the checking of overhead heating in dryers and steamers, less vigorous agitation during padding and the use of defoamers in the padding liquor.
- (d) Pale spots due to residual alkali on the goods. The goods should be treated with acetic acid before dyeing to bring pH at 6.0.

- (e) Coloured specks due to incorrect padding liquor. The dispersion of dyes should be checked and the padding liquor should be properly filtered.
- (f) Ending or tailing due to high affinity of the dyes. The remedies are the use of smaller trough, higher padding speed and combination of dyes of similar affinity.
- (g) Pale shade in intersections due to poor penetration of dye. The fault may be overcome by increasing nip pressure and impregnation time and by using wetting agents.
- (h) Dark or pale selvages may be due to feeding liquor from one side of the trough. The liquor feed should be checked and controlled.
- (i) Fuzzy or frosted dyeing may be caused by colour migration during intermediate drying or the thermosol process. The remedies are the use of migration inhibitor and low wet pick-up.
- (j) Widthways variation in drying may be minimised by checking of air jets and velocity of air circulation in stenter.
- (k) Generation of foam may be caused by the use of excessive dispersing agents and other chemicals in pad liquor. The remedy is the use of suitable defoamers (Jaysynth, 1986).

2.5.6 Colour correction on polyester

Polyester dyeing is highly reproducible if certain standardisation procedures are followed. The three major colour faults are mismatching, uneven dyeing and inadequate fastness. Mismatches may be due to wrong formulation or loss of dye. The dye may also agglomerate or decompose because of unbuffered process water, alkaline dyebath or reduction of dye.

Colour depth may be reduced to a small extent by dropping all or part of the dyebath and setting a new dyebath. At dyeing temperature a new equilibrium is established at lower depth. Small correction additions may also be made in the normal manner. In carrier dyeing at boil, the degree of stripping is small, unless excess carrier is added and the process is prolonged. Under high-temperature conditions, stripping is quicker, but depends on aqueous solubility of the dyes. The degree of stripping can be raised by 30% by adding an ethoxylated product of low cloud point, which provides an external phase capable of dissolving and retaining disperse dyes. The product must be thoroughly removed before redyeing.

For complete stripping, the dye should be destroyed as desorption proceeds using 1–2 g/L caustic soda for 20 min at 125–135°C. Some polyester material may be damaged and some disperse dyes may be unaffected. A milder treatment may also be done with sodium sulphoxalate-formaldehyde and soda ash or zinc sulphoxalate-formaldehyde and acid. The former may be treated in the presence of a carrier at boil at a pH of 4.0–5.0. Many

disperse dyes may be stripped at pH 4.0 (formic acid) with sodium chlorite at boil, but a yellowish ground colour may result. The two treatments may be carried out successively. It should be kept in mind that a long treatment of polyester at high temperature, especially at high pH, is harmful.

2.6 Disperse dyes on texturised polyester

Dyeing of texturised polyester needs some additional precautions and criteria compared with normal varieties of polyester. Scouring, besides removing the impurities, also completes the relaxation shrinkage of the fabric, which is of great importance. Scouring may be carried out in winch or open-width washers. The bath is set at 60°C with 1 g/L anionic detergent, e.g. Lissapol N and 2 g/L soda ash. The temperature is raised to 80°C and the goods are treated for 20 min and washed thoroughly.

The main problem in dyeing of texturised polyester material is barré or a striped dyeing effect. This produces lighter or deeper horizontal lines produced at regular intervals across the fabric width. Besides the barré problem, the texturised materials also produce shade variations at regular intervals across the length and width of the fabric. The dyes are selected on the basis of their ability to cover structural differences or barré. There are several tests like the Rhodiaceta test, Dupont transfer test, BASF methods, etc. The simplest method is to dye at a very light shade and to check uniformity of dyeing visually. The dyeing may be carried out by carrier or high-temperature methods. The carriers, which were developed to accelerate the rate of dyeing of polyester fibre at boil, are found useful in getting barré-free dyeing on texturised polyester due to higher migration of the dyes. The thermosol process affects aesthetic properties such as bulk and texture of the texturised polyester fabric. However, under carefully controlled thermosol conditions, the fabric with satisfactory handle may be obtained.

A few disperse dyes, suitable for dyeing of texturised polyester, are listed below (Subramanian, 1973):

For carrier method:

- C.I. Disperse Yellows 8, 42, 87, 99
- C.I. Disperse Oranges 25, 59
- C.I. Disperse Reds 60, 78, 86, 91, 138
- C.I. Disperse Violets 8, 27
- C.I. Disperse Blues 95, 118, 120.

For high-temperature method:

- All the above dyes and C.I. Disperse Yellow 88, Red 65, Blues 55, 56, 64, 87.

2.6.1 Hank dyeing of texturised polyester

The hanks are to be cross-wound and tension during winding must be uniform and minimal. The hanks are subjected to relaxation treatment by hanging freely under steam at atmospheric pressure for a sufficient time, when they shrink due to release of tension. Due to high bulk of the yarn, it is advisable to put the hanks in cages. The dyeing is preferably done at high temperature using 1 g/L non-foaming anionic levelling agent (Albegal C, ICI), 1 g/L monosodium phosphate and 2 g/L formic or acetic acid. The material is treated in this solution for 10 min and then the dye is added at pH 5.5–6.0. The temperature is raised to 95°C and the treatment is continued for 1 h with carrier for atmospheric dyeing. For high-temperature dyeing, levelness of the dyeing may be checked after dyeing for 15 min at 95°C. If unevenness is due to foam, defoamer is added. The material is run for another 20 min at 95°C, then the temperature is raised to 130°C over 40 min and dyeing is continued for 45 min. The material is subsequently reduction cleared.

For stabilised bulk yarn used in circular knitted goods, stabilisation is not required. All texturised goods shrink, both in width and length, during dyeing, but pre-heat-set (at 175°C) material shrinks six times less in width and twice less in area.

2.7 Disperse dyes on modified polyester

There are several modified varieties of polyester in the market, a few are listed below:

- (a) Lustrous trilobal variety
- (b) Micro polyester fibres
- (c) Easy dyeable polyester (EDP)
- (d) Anionic modified or cationic-dyeable polyester
- (e) Trilobal polyester.

2.7.1 Trilobal polyester

Lustrous trilobal fibres are made by passing the polyester melt through a spinneret having a trilobal (or dog bone) cross-section instead of a circular cross-section. As a result, the surface area for a given weight increases and lustre enhances. The dyeing properties are similar to normal polyester, but more dye is required – about 10% more for pale shades and 20–25% more for deep shades.

2.7.2 Micro and ultra-micro fibres

Generally the linear densities of fine, medium and coarse varieties of polyester fibres are between 1 and 2.4, between 2.4 and 7 and higher than 7 dtex

(denier), respectively. Micro filaments have fineness less than one. The actual dtex per filament is between 0.3 and 0.9 for micro fibres and less than 0.3 for ultra-micro or super-micro fibres.

Lightweight polyester can be produced by the causticisation process. Although it gives a silk-like lustre, the properties required for apparel application, i.e. skin sympathetic and eye-catching, are lacking.

The advantages of micro fibres are:

- Soft and flexible
- Good breathing qualities
- Easy care
- Skin sympathetic
- Eye-catching, velvet touch
- Water repellent
- Higher bulk in the fabric
- Better drape of the fabric
- Weather-friendly.

The disadvantages of micro fibres are:

- High cost
- Very delicate nature
- High covering area
- Lower dye pick-up, more dye required than conventional fibres
- Lower light- and wash-fastness
- Lower productivity, longer washing and drying cycle.

The micro filaments are now well established in many apparel markets – all kinds of sportswear, ladies apparel, bathing suits, men's wear, skiing outfits, wind-cheaters, raincoats, shirts, blouses, scarves, neckties, draperies, etc. Whilst most micro fibres are micro filaments, micro staple polyester (0.45–0.55 dtex) and acrylic (0.55–0.77 dtex) are also produced.

With such a fine denier fibre, certain precautions are to be taken during processing. The processing is preferably to be done under tensionless condition. Scouring should be done with a mild detergent at 90–95°C and washed carefully. For batch processing, the material is circulated at 90°C for 30 min in a bath containing chelating agent, a deaerator and emulsifier followed by hot rinsing and neutralising with acetic acid. Alternately, micro fibres may be scoured and bleached with 3 g/L hydrogen peroxide, 4 g/L soda ash, 2 g/L detergent and required quantity of stabiliser. For continuous processing in open-width washer the fabric is padded with a solution containing a detergent and pH controlling agent and steamed for about 60 s under atmospheric conditions followed by a series of hot rinses.

Micro fibre fabrics are not heat-set before dyeing but can be heat-relaxed to give an even shrinkage and uniform fabric density. However, fabric with 100% PET micro fibre plain warp should be heat-set before dyeing to ensure dimensional stability and finished appearance. Fabric should be handled under minimum tension during heat-setting to maintain optimum softness and suppleness. Heat-setting is done only after the pre-treatment step to avoid curing of sizing ingredients. Heat-setting is done at 180°C for 30–45 s (Kale, 2010).

Micro fibres take up dyes faster and may cause levelling problems. The dyeing should be started at lower temperature (10°C lower than that for normal polyester) and temperature is to be raised slowly (maximum 2.5°C min). The dyeing time at the maximum temperature (usually 130°C) should be at least 30 min for better levelling. Dyestuff with good levelling properties should be used. Due to the very high surface covering and compactness of the packages, beam dyeing should be avoided. Continuous dyeing of polyester micro fibre is not preferred as the fabric cannot achieve desirable bulk. It is advisable to dye the fabric in winch, overflow or jet dyeing machine. Some problems associated with wet processing of micro fibres are (Kale, 2010):

- (a) Due to the large surface area, micro fibres require 2–5 times more fibre processing aids (sizes, oils, antistats, spin-furnishing, etc.) and consequently need an efficient scouring. An emulsifier may be added during dyeing.
- (b) Complete removal of unfixed dyes and chemicals through washing is difficult as large numbers of small interstices are present on the surface area of the micro fibre.
- (c) Level dyeing is difficult due to higher rate of dye strike.
- (d) Deeper shades are difficult to obtain.
- (e) Colour fastness ratings to wet treatments, light and heat treatment are lower.
- (f) The micro fibres fabrics exhibit a much greater rate and extent of shrinkage as the temperature of dyebath is raised.
- (g) Inadequate care in preparation stage may result in abrasion marks and crease marks.
- (h) A powerful anionic dispersing agent stable at high temperature should be added.
- (i) As level dyeing is difficult in micro fibre fabrics, a non-ionic levelling agent in the dyeing bath is preferable.
- (j) A lubricant as anti-creasing agent may be added to the dyebath to remove crease marks.
- (k) An effective deareator is also recommended over a defoamer to remove entrapped air, which otherwise may cause the fabric to float in the dyebath causing further uneven dyeing.

The dyeing properties of polyester micro fibres are quite different from those of conventional polyester fibres. The simple Langmuir sorption isotherm fits well to the experimental sorption isotherms obtained at high dyeing temperatures. The correlation is, however, better for micro fibres than for conventional fibres (Park *et al.*, 2002).

One study (Park and Konkar, 2003) showed that the sorption isotherms of super-micro fibres are not same as those for micro fibres or conventional fibres. This means the dyeing process for super-micro fibres has to be modified. Super-micro fibres can accept more dye and they must be dyed at higher temperature.

A typical recommended dyeing procedure for polyester micro fibre fabrics is as follows (Sekhar, 2001):

1. Set the bath at 60°C with
 - (a) 0.10% anionic dispersing agent
 - (b) 0.20% wetting agent cum emulsifier
 - (c) 0.25% deareator
 - (d) 0.50% levelling agent
 - (e) 1.0% anti-creasing (lubricant) agent
 - (f) $x\%$ acetic acid (to adjust pH 4.5–5.0)
 - (g) Run for 10 min.
2. Add $x\%$ disperse dyes, run for 10 min.
3. Heat the dyebath at the rate of 0.5–1°C/min up to 96°C and run for 20 min.
4. Heat the dyebath at the rate of 0.5–1°C/min up to 130°C and run for 60 min.
5. Cool the dyebath at the rate of 1°C/min up to 71°C and check the sample.
6. Drain.
7. Refill and wash for 10 min at 49–60°C.
8. Drain.
9. Reduction clearing at 70°C with 4 g/L soda ash and 4 g/L sodium hydro-sulphite for 15 min.
10. Rinse and neutralise with 0.5% acetic acid.
11. Drain and unload.

2.7.3 Hollow polyester fibres

The dyeing behaviour of standard and hollow PET fibres was investigated by using azo disperse dyes with three different molecular sizes (Topal *et al.*, 2010). Almost similar dye exhaustion values were obtained between standard and hollow fibres; however, the colour strength (K/S) values of standard fibres were significantly higher than those of hollow fibres. In other words, hollow fibres tend to have lower colour strength when dyeing with a similar

dye concentration due to higher reflectance and brightness values for hollow fibres. The other two reasons for different K/S values are the higher number of hollow filaments on the same sample weight and the different dye penetration behaviour of the fibres. It is also shown that the fibres have similar wash-fastness values when dyeing with the same dye concentration. Special attention must be given to hollow yarns in the dyeing processes since hollow fibres need more dye than standard fibres in order to achieve similar colour strength.

2.7.4 Easy dyeable polyester (EDP)

EDP, e.g. Nirster super (Nirlon, India), has similar density and melting point as normal polyester. However, the glass transition temperature (T_g) is approximately 10°C lower. Hence, disperse dyes show a higher rate of diffusion and can give deep shades at 100°C even without using any carrier. EDP has less pilling tendency than normal polyester. It is more hydrophilic. Weight reduction is possible using caustic soda solution of lower strength than that for normal polyester. The lowering of T_g may be achieved by copolymerisation of polyethylene terephthalate with co-monomers like polyethylene oxide, aliphatic dicarboxylic acid, polybutylene terephthalate, etc.

EDP behaves differently on heat-setting. Normal polyester, on heat-setting, absorbs less dye than unheat-set up to 200°C. With EDP, dye saturation steadily increases with increasing heat-setting temperature. The effect is more pronounced with slower diffusing dyes – opposite to that for normal polyester.

Dyeing of EDP is started at 40°C (pH 5.0) with anionic dispersing agent and the temperature is raised to boil over 40 min. The dye is almost completely exhausted within 30 min at boil and hardly any residual dye is left in the dyebath. The material is given hot and cold wash followed by reduction clearing at 40–50°C and soaping at 70–75°C (Jaysynth, 1987). Many disperse dyes show lower light-fastness (by 1–1.5 grade) and slightly lower wash-fastness (ISO Washing Test No. 3) on EDP.

2.7.5 Cationic-dyeable polyester

Unlike ordinary polyester fibres, cationic-dyeable polyester fibre is a special polyester fibre that can be dyed with cationic dye. Excellent colour development and fastness have enabled cationic-dyeable polyester fibres to be used in many applications. Conventionally, however, they must be dyed at high temperature and pressure, making it difficult to combine them with wool, silk or other natural fibres that tend to lose strength and texture when subjected to extreme conditions. Combination with polyurethane or other elastic fibre is also problematic.

Cationic-dyeable polyester fibres that can be dyed at ambient temperature and pressure exist, but their fibre strength is generally 20–30% below

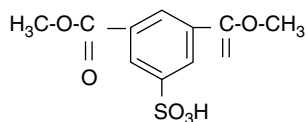
that of ordinary polyester fibres. This weakness complicates their use as differentiated yarns, such as highly multi-filament or non-circular cross-section yarn, so applications and compatible materials are limited. Polyester fibre producer Teijin Fibers Limited, Japan announced on 22 April 2010 in Osaka the development of a new cationic-dyeable polyester polymer, called V4, which can be dyed at ambient temperature and pressure and also offers excellent fibre strength and dyeability.

Dacron 64 (staple fibre) manufactured in 1958 by Dupont was the first modified polyester fibre having affinity for basic or cationic dyes (cationic-dyeable polyester, CDP). Later Dupont manufactured trilobal filament, Dacron 62, from the same polymer. Both CDPs are manufactured by introducing about 1–3% sodium-5-sulphoiso-phthalic acid into polyester during trans-esterification or polycondensation reaction whereby it becomes a part of the polymer (Gulrajani, 1975). In India, CDP is produced only in dimethylterephthalic acid base and not in terephthalic base. The fibre is made by charging sodium 5-sulphodimethyl-isophthalate (Fig. 2.5) into dimethylterephthalate (Fig. 2.6).

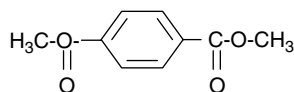
The property of CDP to absorb basic dyes is of practical significance in finishing. As the dyes are held by ionic bonding, the shades remain unaltered in resin finishing and no thermal migration occurs as in normal polyester finishing.

In addition to basic dyes, CDP is also dyeable with conventional disperse dyes. Unlike EDP, disperse-dyed CDP does not show lowering of washing and light-fastness. CDP finishing follows the normal sequence as per conventional polyester.

Disperse dyes, in general, have higher affinity for CDP than normal polyester. For some dyes, light-fastness is slightly lower on CDP. 4–6 g/L Glauber's salt is employed in the dyebath to protect the fibre. The pH should not be below 4.0, otherwise the hydrolysis of the fibre may occur. For colour fixation, the highest temperature recommended is 120°C. If cationic dyes are simultaneously used for brightening in carrier method of dyeing, the carrier should be non-ionic in nature. The material is rinsed, reduction cleared with soda ash (2–3 g/L), sodium hydrosulphite (2 g/L) and non-ionic detergent for 20 min at 70–80°C. The goods are rinsed warm and acidified with acetic acid.



2.5 5-Sulphodimethyl-isophthalate.



2.6 Dimethylterephthalate.

The scoured, bleached and heat-set CDP fabric can be dyed with basic dyes in an HT/HP dyeing machine using:

- 2 g/L sodium acetate
- 3 g/L sodium sulphate and
- 0.1 g/L retarding agent.

The temperature is raised from 30°C to 115°C at the rate of 1°C/min. After dyeing for 45 min, the dyed samples are rinsed and washed with 2 g/L non-ionic detergent at 60°C.

2.8 Disperse dyes on nylon

As disperse dyes are held by physical bonding forces, the dyeing is unaffected by the structural variations, i.e. variations in end amino groups of nylon. Disperse dyes are, therefore, preferred for nylon having distinct barré. The application method is simple and the dyeing is level. However, most of the disperse dyes have moderate affinity for nylon, moderate light fastness and low washing fastness, particularly in heavy depths. The washing-fastness to ISO Washing Test No. 3 at 60°C is inadequate in most cases. The dyers, therefore, prefer acid and metal-complex dyes for nylon in spite of their poor coverage to barré.

The dyebath is set at 30°C with 1 g/L non-ionic dispersing agent and 0.5 g/L sodium hexametaphosphate and the pH is set to 6.0–7.0. The selected disperse dyes are dispersed in warm water and appropriate dispersing agent, sieved and added to the pre-set dyebath. The temperature is raised at 2°C/min for simple disperse dyes and 1°C/min for high-molecular dyes to near boil and maintained at that temperature for a minimum of 45 min before sampling. Once the desired shade is attained, the material is rinsed cold and soaped with 1 g/L non-ionic detergent at 40°C for 10 min and finally rinsed cold.

The low-molecular weight, good levelling disperse dyes are widely used for dyeing of nylon hose and tights, carpets and woven and warp-knitted fabrics, whenever end-use requirements do not require high wash-fastness. Low-molecular-weight disperse dyes cover chemical variations present in the fibre, but they are sensitive to fine structural differences like those occur in texturised materials. The washing and sublimation fastness properties are better, but migration and levelling properties are poor. A typical trichromatic combination of high-molecular-weight disperse dyes that proved satisfactory under commercial processing conditions consists of the following three dyes:

1. C.I. Disperse Yellow 27
2. C.I. Disperse Red 91
3. C.I. Disperse Blue 83.

Other disperse dyes suitable for nylon exhibiting good light-fastness are:

1. C.I. Disperse Orange 30
2. C.I. Disperse Reds 50 and 60
3. C.I. Disperse Blue 56.

2.9 Disperse dyes on other fibres

Disperse dyes can be used to produce light to medium deep shades on acrylic and modacrylic fibres. The dyeing mechanism and process correspond to those used on polyester and cellulose acetate fibres. However, dyeing is to be performed below 100°C. Addition of carriers is not required. The good migration properties of disperse dyes result in problem-free level dyeing.

Poly (vinyl chloride) (PVC) fibres, are characterised by their flame retardance. They are dyed preferably with disperse dyes. As with modacrylic fibres, high temperatures must not be used because of shrinkage of the PVC fibre. Hence, some fibres are dyed at 60–65°C with dyeing accelerants. Other PVC fibres can be dyed at 100°C without a carrier and a few even at 110°C. Dyes must be selected with regard to the light-fastness desired.

Elastomeric polyurethane fibres are used in stretch articles and in knitted fashion materials. Light shades can be dyed tone-on-tone on polyamide-polyurethane mixtures with disperse dyes at 95–98°C and pH 6.0–7.0. However, the wet-fastness on polyurethanes is lower than on polyamide. Because of the temperature sensitivity of polyurethane fibres, mixtures of elastomeric and polyester fibres must be dyed with small molecular, rapidly diffusing disperse dyes for 30 min at 120°C according to the HT process. Modified PES fibres that are dyeable at 100°C without a carrier are often used in mixtures with elastomeric fibres. In all dyeing processes for elastomeric fibres, dyeing equipment that permits low-strain guidance of the material and the lowest possible thermal stress are important (Hunger, 2003).

2.10 Dyeing of nylon fibres

The dyeing characteristics of nylon are influenced by two important fibre characteristics, namely:

- (a) Amino end-group content and
- (b) Physical structure – internal and surface.

The variation of lustre may be due to differences in internal structure, surface characteristics or both. If only surface characteristics vary, then, even if identical amounts of dye are present in the fibres, the apparent depths may be different.

Four simple dyeing tests are recommended (Nunn, 1979) to find the cause of unevenness or non-uniformity in dyed nylon, namely:

- (a) Dyeing with 0.33% C.I. Disperse Blue 56 at 85°C for 45 min in the presence of 1 g/L non-ionic dispersing agent. Any unevenness in dyeing will be due to lustre difference as the dye is insensitive to the other two causes.
- (b) Dyeing with 5.0% C.I. Acid Blue 45 at 100°C for 1 h in the presence of 4.0% formic acid (90%). The dye is very sensitive to differences in end amino groups. It is also relatively sensitive to lustre variation and slightly sensitive to physical differences.
- (c) Dyeing with 2% C.I. Direct Blue 74 at 100°C for 1 h in the presence of 3.0% acetic acid (90%). The dye is very sensitive to both differences in end amino groups and physical structure. It is also relatively sensitive to lustre variation.
- (d) Dyeing with 10% Multamine Black B (mixture dye developed by ICI) at 85°C for 45 min in the presence of 1 g/L non-ionic dispersing agent. It is very sensitive to lustre differences and mostly insensitive to the other two factors.

‘Equivalent weight’ for chemical compounds (or polymer) is defined as that weight which contains one gram-equivalent weight of the component taking part in the reaction. For example, hexamethyldiamine has two amino groups and an approximate molecular weight of 116.2. The equivalent weight in terms of its reaction with acid is $116.2/2$ or 58.1. Alternately, 1 gram will be the equivalent of $1/58.1$ amino group, which may be expressed as $1/58.1$, i.e. 17.2×10^{-3} eq/g or 17.2 milli eq/g or 17.2×10^2 mili eq/kg or 17.2×10^3 eq/ton.

2.10.1 Amino end-group analysis

The amino end-groups in nylon are determined by the titration method. 50/50 methanol/phenol mixture is prepared and after adding 1 g of nylon sample to 50 mL of the solution it is refluxed in a water bath for about 2 h (until the nylon dissolves completely). After cooling, the flasks are removed from the water bath. This solution is titrated against 0.02 N HCl using Bromothymol Blue indicator. The indicator solution is prepared by dissolving 0.1 g Bromothymol Blue in 20 mL methanol, 4.3 mL 0.5 N sodium hydroxide solution and distilled water to make the total volume to 50 mL.

A blank titration is carried out using 50 mL of methanol/phenol mixture. The refluxed samples are then titrated with 0.02 N HCl using Bromothymol Blue indicator, the end-point being blue to red. This experiment is done in triplicate.

$$\text{Amine end groups (meq/kg)} = (A - B) \times N \times 1000 / \text{weight of sample [2.2]}$$

where, A = vol of 0.02 N HCl in mL for sample.

B = vol of 0.02 N HCl in mL for blank.

N = normality of HCl solution

2.10.2 Carboxyl end-group analysis

About 1 g of nylon is dissolved in 25 mL benzyl alcohol by refluxing in a water bath for 30 min. The contents are then titrated with 0.02 N alcoholic KOH using phenolphthalein indicator. A blank titration is carried out with 25 mL benzyl alcohol.

$$\text{COOH end groups (meq/kg)} = (A - B) \times N \times 1000 / \text{Weight of sample [2.3]}$$

where, A = mL of 0.02 N KOH for sample.

B = mL of 0.02 N KOH for blank.

N = normality of KOH solution.

For textile-grade, regular-dyeing nylon 6 yarn, the quantity of amino and carboxyl end-groups is about 60 eq/ton. The amino end-groups in nylon 6 have a predominant effect on dye pick-up when dyed with acid dyes, as shown in Table 2.3 (Gupta and Kothari, 1997).

With today's nylons, barré due to variation in amine end-groups or dye sites is rare. Most dye-related problems are now due to differences in fibre porosity, which determines accessibility of the dye sites. Porosity is determined by the total tension-temperature history of the fibre – during fibre manufacturing, texturising, heat-setting, dyeing and finishing. Variations in porosity determine the rate of dyeability with dyes, especially those of high molecular weight, namely milling acid, metal-complex and direct dyes. Because of the increasing demand for higher wash-fastness, the dyer is often forced to use rate-sensitive dyes.

Water has pronounced effects on the processing and performance of nylon. For instance, nylon fabrics can be set with moist heat at 93–121°C, far below the temperature of 196–210°C necessary to set the same fabric with dry-heat.

Table 2.3 The relationship between pick-up of acid dyes and amino end-groups content in nylon 6

Amino end-group content (eq/ton)	Dyeability with acid dyes
10–15	Light
35–45	Regular
80–90	Deep
95–100	Ultra deep
115–120	Super ultra deep

In sharp contrast, water or moisture has very little effect on the heat-setting of polyester, which is dry-set at 180°C or more. Furthermore, once set, nylon, for all practical purposes cannot be reset, while polyester can be set repeatedly by using successively higher temperatures. Thus, nylon 6,6 and polyester differ dramatically in their response to moisture and heat-setting, though their softening (235°C) and melting points (250°C) are very similar. Nylon, of course, has moisture-sensitive hydrogen bonds, which are absent in polyester.

The potent carrier activity of water on nylon was studied (Holfeld and Shepard, 1978). The concept of water as a carrier for nylon is not, in itself, new. However, it is often overlooked because carriers are generally considered chemical compounds like phenols, chlorinated hydrocarbons, esters, etc., whereas we cannot even think of water as a chemical. Carriers can be considered as compounds, which provide chemical energy to supplement and/or replace thermal energy in the dyeing and finishing of thermoplastic fibres. Water provides chemical energy equivalent to about 100°C of dry thermal energy in its effects on a variety of nylon fibre properties. The T_g of nylon 6,6 at 0% RH is about 80°C based on measurement of films. At 100% RH, T_g is -10° to -20°C, i.e. lowered by about 90–100°C. Water has much less effect on polyester, generally equivalent to about 20°C of thermal energy. The concept of chemical energy/molecular lubrication effect of water on nylon helps to explain better the overall behaviour of nylon and the differences between the responses of nylon and polyester.

Nylon is dyed by a hybrid mechanism. Works with crimper box barré induced in stuffer box texturing and false twist barré induced in false twist texturing showed that all types of dyes – disperse, levelling acid and high-molecular milling acid dyes – are sensitive to the same structural features. This evidence led to the conclusion that the initial attachment of all types of dyes on nylon is by disperse dye mechanism. Acid dyes subsequently exchange ions with end amino groups and then transfer or level, if possible. The end amino groups are necessary primarily to provide good wet-fastness.

Acid dyeing of nylon is analogous to precipitation reaction. The formation of slightly soluble precipitate of disperse and levelling acid dyes, or insoluble precipitates of milling acid dyes, drives the reaction to equilibrium. An essential role of pH in this hypothesis is to convert acid dyes to the unionised disperse species which are insoluble in water but soluble in organic solvents such as nylon. End amino groups are not essential for acid dyeing of nylon, provided the dyes used have adequate fastness. They are necessary only to prevent the precipitate (on dyed nylon) from redissolving.

Nylon fibres contain both amine and carboxylic acid terminal groups, and by selecting the appropriate dyeing conditions, the uptake of both anionic and cationic dyes may be favoured. Nylon can also be readily dyed with disperse dyes. Thus, virtually all the major classes of dyes are substantive to nylon and there is an extremely wide range of dyes available for their coloration.

It is widely presumed that, under acidic conditions, the dyeing of polyamide fibres with anionic mono or polysulphonated dyes (acid dyes) is described by an electrostatic attraction between the anionic dye and the protonated, hence cationic, fibre. Dyeing of wool or nylon, for example, is normally achieved by applying these dyes from weakly acid solution at the boil; however, colour chemists quickly realised that anionic dye molecules were not absorbed solely by ionic interactions and solvophobic or hydrophobic interactions are also important. Hydrophobic interactions were employed to describe the phenomenon of nylon 'overdyeing'. Analysis showed that highest overdyeing was observed with mono-sulphonate dyes, followed by disulphonate and trisulphonate. The tetrasulphonate dye, C.I. Acid Red 41, showed no tendency to overdy. However, hydrophobic interactions break down above 60°C. As all the above dyeing processes were carried out at boil, it is, therefore, proposed that aromatic or π - π electrostatic interactions are largely responsible for these effects. In case of nylon 6 and nylon 6,6, it has to be noted that there are no aryl groups present in the fibre and thus, at first sight, π - π interactions of the dye with the fibre are not possible. However, dyed fibre is a different substrate, as absorbed dye possesses aryl groups capable of undergoing π - π interactions with newly absorbed dyes (Lewis, 1998).

2.11 Anionic dyes on nylon

Acid dyes are now widely used in the dyeing of nylon and it has been suggested (Stead, 1975) that as rough guidelines, adequate wash-fastness and level dyeing on this fibre will be achieved if the molecular weight does not fall below 400–500 for mono-sulphonated, and about 800 for disulphonated dyes. If the molecular weight is raised above these values, unlevel dyeing behaviour ensues, whereas if the molecular weight is lowered, the wash-fastness properties suffer. In a series of mono-sulphonated alkylaryl amino anthraquinone dyes, a similar linear relationship exists between the standard affinity for nylon and the number of carbon atoms in the alkyl group up to a value of four (Lewis, 1998).

Acid dyes exhibit significantly better wet-fastness on nylon than on wool and it is found convenient to modify the classification system for acid dyes, which was earlier based on wool. Considering the dyeing behaviour and affinity of acid dyes for nylon, the dyes may be divided into three subgroups (Nunn, 1979) – Groups I–III.

Group I: Dyes with low affinity under neutral or weakly acidic conditions, but exhaust well on nylon under strong acidic conditions.

Group II: The largest group of acid dyes, which exhaust well on nylon within pH range 3.0–5.0.

Group III: Dyes, which exhibit high affinity for nylon under neutral or weakly acidic conditions (pH 5.0–7.0).

Although nylon 6,6 and nylon 6 exhibit many similarities, there are significant differences in their physical and to a lesser extent, chemical characteristics, which are to be considered while selecting dyes and processing techniques. Due to more crystallinity, nylon 6,6 shows slower rate of dyeing and slightly superior fastness in comparison with that of nylon 6 dyed with the same dye in equivalent depth. The dyes build up more readily on nylon 6 and show superior levelling properties.

The more compact structure of nylon 6,6 restricts migration and levelling of dye molecules – the dyes should be more carefully selected and better controls are to be exercised in the dyeing process. Generally dyes of larger molecular size are selected for nylon 6 for better fastness. Although the presence of antioxidants, delustrants, ultraviolet stabilisers and fibre lubricants may influence light-fastness of dyes, the effects are same on both fibres. A specific dye at a given depth on both fibres shows identical light fastness.

It is preferable to dye nylon with dyes of moderate affinity, i.e. Group II dyes. These dyes exhibit good levelling and migration properties and reasonable coverage of structural variations. These less complex dyes provide combinations of good light-fastness (5–6, 6) and also good wet-fastness (ISO Washing Test No. 3) in pale and medium depths on nylon 6,6. However, on nylon 6 it is often necessary to after-treat medium depth dyeing with synthetic tanning agents (syntan) in order to achieve comparable fastness. For heavy depths, it is frequently necessary to use large-molecular-weight neutral-dyeing (Group III) dyes and in most cases to employ a synthetic or full back-tanning after-treatment. Though a wide range of acid dyes are available, it is not easy to find dye combinations, the individual components of which are truly compatible with respect to their dyeing rates, migration, light- and wet-fastness. Only a limited number of red dyes of neutral affinity (Group III) have good light-fastness (≥ 5). To achieve high light-fastness (6–7 or 7) as in the case of upholstery, it is often necessary to supplement the range of acid dyes with metal-complex dyes.

Typical trichromatic combinations of weakly acidic (Group II) and neutral affinity (Group III) dyes are as follows:

Group II: C.I. Acid Yellow 25, C.I. Acid Red 57 and C.I. Acid Blue 72

Group III: C.I. Acid Orange 127, C.I. Acid Red 299 and C.I. Acid Blue 138.

2.11.1 pH controlling agents

Control of temperature and pH are the most important factors in the dyeing cycle with respect to level and reproducible dyeing. The pH of a dyebath

may change during dyeing process due to absorption of acid by the fibre itself, increased alkalinity during boiling of temporarily hard water and/or reduced alkalinity due to decomposition of ammonium salts.

The control of pH in the dyeing of polyamide fibres with acid dyes is accomplished by three fundamentally different techniques (Kamat and Borkar, 1993):

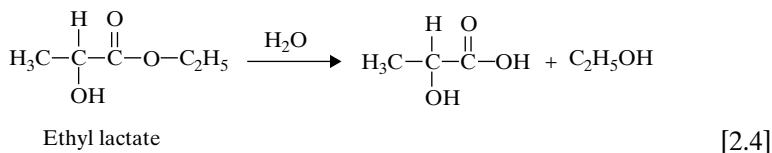
1. Maintenance of a relatively high degree of acidity.
2. Control of pH within narrow tolerances.
3. Gradual pH sliding towards acidic conditions as dyeing proceeds.

Approach (1) is normally the simplest and most straightforward, and is used in the application of levelling acid dyes. The agents traditionally used are sulphuric acid or formic acid.

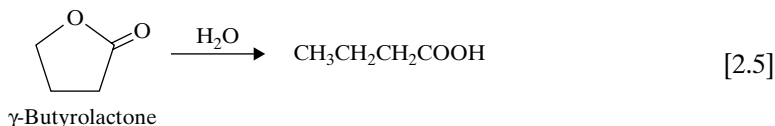
Approach (2) requires much greater knowledge of the internal factors that not only determine pH, but also those which stabilise it. The pH of the water supply may vary or drift during heating and thus a buffer system is required that resists the effects of extraneous influences. This system is usually based on two chemicals, namely a weak acid and its salt, with a stronger base such as acetic acid–sodium acetate or phosphoric acid–sodium phosphate. In a phosphate buffer system, a mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate is used, since these salts are easier to handle and small weighing errors do not have a significant effect on the pH of the final mixture. This system is most useful near pH 7. It is unsuitable for use as a buffer at pH values below 6.0 and above pH 8.0 (Dawson and Robert, 1979).

Approach (3) is particularly useful for non-migrating acid dyes on nylon. The controlled lowering of the pH can be achieved by using products that release more acidic compounds as they undergo decomposition as the dyeing temperature increases. Typically, these include ammonium salts (e.g. sulphate, acetate, tartrate, etc.) with the most widely used being ammonium sulphate, since it consists of salts of a strong acid with a weak base. At boiling temperatures, ammonium sulphate decomposes gradually liberating ammonia and sulphuric acid, a strong acid that subsequently lowers the pH as the ammonia escapes. However, in enclosed or partially enclosed machines this system is not very efficient because ammonia is prevented from escaping.

An alternative method for obtaining a pH that slides in the direction of acidity is to use organic esters that hydrolyse to alcohol and acid under the conditions of processing. The Estrocon process in 1953 recommended the use of hydrolysable esters diethyl tartrate or ethyl lactate for dyeing wool with acid milling dyes and chrome dyes by the single-bath method – the reaction is shown in Equation [2.4] (Hannay and Major, 1953).



In the 'Sandacid V' process (Sandoz, 1977), γ -butyrolactone undergoes hydrolysis to produce butyric acid is shown in Equation [2.5].



Although this procedure is technically sound, it is not widely used, probably because of the increase in processing costs. However, recently there has been a renewed interest in the use of hydrolysable esters, particularly in the application of high-fastness dyeing and dyebath reuse systems (Bide *et al.*, 1997).

The use of hydrolysable organic esters as acid donors for pH control offers distinct advantages in the dyeing of polyamide with acid milling dyes especially in a closed dyeing system. In comparison with ammonium sulphate and sodium dihydrogen phosphate, small quantities of hydrolysable organic esters provide an effective pH sliding. These organic esters (γ -butyrolactone, ethyl lactate and diethyl tartrate) showed higher percentage dyebath exhaustion than ammonium sulphate and sodium dihydrogen phosphate in closed dyeing systems. In addition, the hydrolysable organic esters exhibit very low conductivity of less than 0.5 ms, while ammonium sulphate and sodium dihydrogen phosphate give high conductivity. Since ammonium sulphate exhibited higher conductivity than other acid donors, the large amount of salt present in the dyebath could cause dye aggregation and result in unlevel dyeing. In the early stages of dyeing, the dyebaths containing hydrolysable organic esters exhibited a relatively low rate of exhaustion but a high final exhaustion due to their high initial and low final dyebath pH (Koh *et al.*, 2001).

2.11.2 Levelling and blocking agents

Although control of pH and temperature promote level dyeing, these measures cannot overcome barré dyeing and the use of dyeing auxiliary is essential. For all dye-fibre systems, unlevelness may be two types – 'throughout the substrate' due to faulty dyeing or 'localised' due to non-uniformity of the substrate. Dyeing unevenness in nylon may belong to the second category, i.e. due to barré resulting from variation in amino group.

In 1950s, anionic levelling agents were introduced either as addition to the dyebath or as a pre-treatment of the nylon substrate, prior to dyeing, to promote both levelness and coverage of fibre irregularities. Such anionic levelling or 'blocking' agents are substantive towards the fibre and they compete with the anionic dye for sites on the surface and within the fibre. However, due to stronger attraction of the dye, after adsorption they are slowly displaced by the dye anion. Thus, such agents reduce the initial rate of dye uptake. As the number of available sites is reduced by their adsorption, the relative saturation of the fibre, S_{rel} (i.e. ratio of the number of dye in the system to the number of sites in the fibre), increases, thereby improving dye levelling. The affinity of the levelling agent and dye must be matched in order to achieve optimum results. Typical anionic agents are ethoxylated alkyl disulphonates – polycarboxylic acid levelling agents are also in use.

Anionic blocking agent, Matexil LA-NS (ICI) is applied at 40°C at pH range 4.5–6.5 on nylon 6,6 and at pH range 5.5–7.5 on nylon 6. For level dyeing, when the presence of gross affinity variations is suspected, nylon is treated before dyeing with an anionic blocking agent (3–4%) under acidic conditions (pH 3.0–5.0) for 30 min at the elevated temperature. For less severe variations, the pre-treatment may be made for 20 min at 50°C at normal dyebath pH. These are preferentially absorbed on the fibres, which have more readily accessible amine end-groups. The material is then rinsed and dyed in the usual manner. During dyeing, the majority of blocking agents is gradually displaced by the acid dyes, which have higher affinity for the fibre. Products with good neutral affinity suitable for simultaneous (during dyeing) application are also developed.

Cationic surfactants were introduced to promote the level dyeing of nylon fibres with acid dyes. Early cationic agents were strongly cationic – they were suitable for direct dyes but in case of acid dyes careful dye selection was necessary. Earlier it was thought that anionic dye and cationic agent form a complex which is adsorbed on to nylon substrate as non-ionic species. But later it was realised that the complex reduces the rate of dye uptake. The complex dissociates with increasing temperature, thereby gradually releasing dye anions for adsorption on to the fibre. Weakly cationic agents, typically obtained by the polyethoxylation of alkylamines are commonly employed to avoid precipitation of the complex, acting as a mixture of a cationic and a non-ionic surfactant. In fact, the oxyethylene chain of the cationic agent acts as a solubilising agent for the complex. Non-ionic surfactants are also employed as levelling agents in dyeing of nylon with anionic dyes.

Affinity variations can be minimised by dyeing at high temperature – 110–115°C for nylon 6 and 110–120°C for nylon 6,6. This is due to swelling and increased accessibility in the crystalline region. The rate of dye uptake and migration are significantly higher and the coverage of variations is often significantly improved. Dyes of low-molecular weight are to be selected if

the required wet-fastness is to be achievable. Affinity variations can also be minimised by selecting less critical dyes.

On fibres having no structural variations, selection of dyes of low affinity and good migration properties will favour level dyeing. However, for better wet-fastness, the use of more complex high-affinity dyes may be necessary.

Heat-setting under tension increases crystallinity and reduces the rate of dye uptake, whereas steam-setting has opposite effect on dyeing. A pre-treatment with an anionic blocking agent reduces dye uptake of most acid dyes.

The rate of dye uptake may be decreased by reducing the rate of temperature rise. For dyes of low to moderate affinity, the temperature may be raised at 2°C/min from cold to maximum temperature (85–100°C). For dyes of high affinity, the rate may be reduced to 1–1.5°C/min. In fact, dyes do not exhaust uniformly over the whole temperature range and maximum affinity is exhibited within a small band (50–70°C). The temperature may be increased rapidly below the critical zone and then the temperature is raised slowly (1°C/min) in the critical zone.

The choice of dyebath pH is governed by the affinity of the specific acid dye, but higher the pH, lower is the dye uptake rate and the final dyebath exhaustion. For high-affinity dyes, it is preferable to use acid-liberating salt instead of free acids. The salts enable lower exhaustion rates in the critical zone. At higher temperature, the pH progressively decreases. Sometimes, buffered dye liquors are preferred to ensure reproducibility.

In addition to blocking agent, the use of levelling agents may be necessary. In the presence of levelling agents, shading additions may be done even at high temperature. The performance of a specific levelling agent depends on several factors. Some levelling agents are also effective in correcting unlevel dye batches by treating at boil with 2 g/L levelling agent at pH between 9.0–11.0. Under these conditions most acid dyes are partially stripped from the fibre and can then be exhausted more uniformly, by gradual reduction of the pH of the dyebath, or by redyeing in a fresh bath.

Direct dyes can also be applied on nylon in a manner similar to acid dyes. However, most direct dyes are of limited value for nylon, due to their sensitivity to structural variations or because they offer no significant advantages over acid dyes. Nevertheless, selected direct dyes are economically more attractive to produce full bright reds, scarlets, dark browns, greens and blacks. They exhibit good affinity for nylon under neutral or weakly acidic conditions. The dyeing may be carried out with acid-liberating salts or in heavy depths with acetic acid added gradually to reduce pH. Wet-fastness can be improved by after-treatment. Light-fastness varies from moderate (3–4) to very good (6–7). A few typical direct dyes of value on nylon are:

- C.I. Direct Yellow 19
- C.I. Direct Red 75

- C.I. Direct Blues 74, 189
- C.I. Direct Brown 58.

Chrome dyes can be used to produce economical heavy dyeing on nylon with excellent wet-fastness and good to very good fastness to light. Generally they give good coverage of physical variations, but are sensitive to differences in chemical affinity. The colour matching is difficult as the shade changes after metallisation. Moreover, residual chromium may cause skin irritation. Therefore, these dyes are gradually being replaced by milling acid dyes, which possess adequate fastness.

1:2 metal-complex dyes have proved particularly attractive for dyeing nylon due to high saturation values (excellent build-up properties), freedom from blocking effects (good compatibility in combination shades) and very good fastness properties (washing and light). However, their dyeing characteristics and coverage for affinity variations vary significantly and depend on the molecular size and shape and the number of solubilising groups. Indeed, some 1:2 metal-complex dyes have no solubilising groups and are applied in dispersed form. Due to high-molecular complex structure, 1:2 metal-complex dyes accentuate physical affinity variations in nylon. Nevertheless, the rate of uptake of dye can be controlled by temperature and pH of the dyebath, and by the use of suitable levelling or retarding agents. High-temperature dyeing is advantageous for improving the coverage of affinity variations. The shades are relatively dull, particularly in the red and blue region. A number of acid, metal-complex and disperse dyes enhance the resistance of nylon to thermal and photo-degradation. Very marked protection is given by the following dyes:

- C.I. Acid Yellow 119
- C.I. Acid Red 228
- C.I. Acid Green 43
- C.I. Acid Brown 19
- C.I. Disperse Yellow 50.

Whereas harmful effects are observed with the following dyes:

- C.I. Acid Orange 92
- C.I. Acid Reds 211, 225, 226
- C.I. Disperse Black 1.

The 1:2 metal-complex dyes exhibit good wash- and light-fastness properties, which can be further improved by an after-treatment. During dyeing, strongly cationic auxiliaries are to be avoided as they form low-solubility complexes. There is a wide choice of 1:2 metal-complex dyes offered by several manufacturers differing in the optimum pH range over which they are applied.

1:1 metal-complex dyes are applied under strongly acid conditions. Such conditions can cause degradation of polyamide, thereby limiting the use of 1:1 metal-complex dyes for dyeing of nylons. Nevertheless, selected such dyes can be applied on nylon at pH between 4.0 and 6.0, whenever depth of colour and washing-fastness are of major importance. Ideally, the dyes should be applied as self-colour on nylon as compatibility between the members of this group is poor. A few 1:1 metal-complex dyes attain good wash-fastness in medium to heavy depths and are fast to steam treatment up to 15 lb/in² (121°C), hence can be applied for garments and half-hose.

Dyeing methods

The general procedure for exhaust dyeing of nylon with acid dyes is to adjust the pH of the dyebath between 3.0 and 5.0, according to the depth of shade and the nature of the dye. It is often advantageous to add a levelling agent. The addition of an anionic levelling agent like Lyogen PA 66 (anionic sulphonated oil derivative, Clariant) gives satisfactory level dyeing on barré material with levelling type acid dyes. The method may be used for other classes of dyes on non-barré material. Lyogen PA 66 has affinity for nylon, hence it saturates active sites in the fibre. It can, therefore, be termed as 'anionic blocking agent'. The dyebath is set at 50°C with 4–2% Lyogen PA 66 liq. and acid/acid liberating salt depending on dye class as mentioned below:

- (a) 1–3% acetic acid (80%) for weakly acid-dyeing dyestuff, e.g. Nylosan E and F (F = better wash fast) (Clariant) in medium and dark shades.
- (b) 2–4% ammonium acetate for neutral-dyeing milling acid dyes (e.g. Nylosan N, Clariant), 1:2 metal-complex dyes (e.g. Lanasyne, Clariant), solar (light-fast direct dyes, Clariant) or for light shades of Nylosan E and F.
- (c) 1–2% formic acid for strong acid dyes like C.I. Acid Yellow 17, Red 1, etc.

(The amounts are o.w.m., the lowest and highest amounts are for lighter and darker shades, respectively.)

The goods are worked at this temperature for 15 min. If the barré is pronounced, the temperature may be raised and kept at boil for 20 min followed by cooling to 50°C. The dye is dissolved with hot water, boiled for short time, if necessary, filtered and added in the dyebath. The temperature is then raised to boil in 30 min and dyeing is continued at boil for 60–90 min. The dyestuff for shading and further acid, if required, may be added without cooling, with prior addition of 0.5–1.0% Lyogen PA 66.

With higher barré and especially with high-affinity high-molecular-weight acid and metal-complex dyes, the above process may not give satisfactory results. It may be necessary to pre-treat the material with 3% anionic

blocking agent and 1% acetic acid (pH 5.0) for 30 min at boil followed by rinsing prior to dyeing.

The dyebath is then set with:

- 1% anionic blocking agent
- 2–3% amphoteric levelling/retarding agent
- 3% ammonium acetate
- x % dye and if necessary,
- 0.5% sequestering agent, e.g. EDTA and/or
- 0.2% antifoaming agent.

The temperature is raised to boil over 30 min and treated at boil for 60 min.

For economical reasons, separate pre-treatment with anionic blocking agent is omitted in most of the cases. Instead, the concentration of anionic blocking agent in the bath may be increased to 2–3% and the material is pre-treated in the bath for 20 min at 40°C before the addition of dye and the levelling/retarding agent. If acetic acid is added along with the blocking agent, it is to be subsequently neutralised and pH is to be raised to 6.0–7.0 using ammonia (25%). The pre-treatment enables the blocking agent to be adsorbed on to areas of high affinity and to reduce the effect of affinity variations. The dyeing is then continued in the usual manner. The simultaneous addition of anionic blocking agent and cationic levelling or retarding agent should be avoided since they form a complex with each other. The cationic agents should not be added until the fibre has adsorbed the anionic blocking agents.

The milling acid dyes (e.g. Nylosan N) and 1:2 metal-complex dyes (e.g. Lanasyne) are applied in near neutral bath using ammonium sulphate. For these dyes, the pre-treatment with anionic blocking agent is carried out at the minimum liquor ratio at boil for 30 min followed by addition of cold water to lower the temperature at 65–70°C and pH is raised from 5.0 to 6.0–7.0 by addition of liquor ammonia (25%). Then Sandogen NH (a weakly cationic retarding agent, Clariant) and dye are successively added.

Nylon absorbs dye at relatively low temperature because of the potent carrier action of water on the fibre structure. Selected levelling type of acid dyes can be exhausted to deep shades and have acceptable barré coverage at temperatures as low as 65°C with an appropriate anionic blocking agent. Some of the dyes suitable for low-temperature dyeing of nylon are:

- C.I. Acid Yellows 49, 116, 128, 159, 174, 198
- C.I. Acid Reds 151, 266, 299, 337
- C.I. Acid Blues 25, 40, 78.

At this temperature, nylon fabrics do not hydroset and heat-setting may be carried out under controlled conditions after dyeing.

Since low-temperature dyeing of nylon is a non-levelling system, it requires more care than boiling dyebath methods including the use of best levelling dyes and the optimum retarder.

Chrome dyes are normally applied on nylon by after-chrome method using acid-liberating salts (ammonium sulphate or acetate) at boil. After dyeing for 1 h at boil, formic acid is added gradually to reduce pH to ensure high degree of exhaustion. The dyed material is then rinsed thoroughly and treated in a separate bath containing appropriate amounts of formic acid and sodium (or potassium) dichromate for 45 min at boil. Unlike wool, nylon fibre cannot reduce dichromate ions into chromium ions. Hence a reducing agent like sodium thiosulphate is added in the bath and the treatment is continued for a further 20–30 min.

After-treatments

To achieve optimum improvement in wet-fastness, it is necessary to form a skin around the outer surfaces of the fibre during the above 'full back-tanning treatment'. This is dependent on the concentration of tannic acid, the time and temperature of treatment. For nylon 6,6, the optimum temperature range is 85–95°C, whereas for nylon 6, the range is between 55 and 75°C.

The acid dyes should be fully exhausted and well rinsed. Then the treatment is carried out in a fresh bath containing (% o.w.m.) 2% tannic acid and 2% formic acid (85%).

The temperature is raised slowly to 90°C for nylon 6,6 or 70°C for nylon 6 and the goods are treated for 30 min. Two per cent tartar emetic (potassium antimonyl tartrate) is added to the liquor and the treatment is continued for a further 20 min at the specified temperature. The fabric is thoroughly rinsed and dried.

When applied correctly the full back-tanning treatment results in marked improvement in wet-fastness of dyes. However, the process has several disadvantages:

- (a) Pure tannic acid is costly. The yellow impurities present in it may stain the fibre by absorption. During alkaline washing also, the material may become yellowish due to oxidation of tannic acid.
- (b) Potassium antimonyl tartrate is toxic.
- (c) The treatment may reduce light-fastness of the dyeing.
- (d) Two-stage treatment is expensive.
- (e) The treatment is not stable to steam or heat treatment.
- (f) A harsh handle to the fibre may be imparted.

Full back-tanning treatment is therefore restricted to heavy, dull colours such as brown, navy and black. The after-treatment may be carried out on any material dyed with anionic dyes. However, the application is mostly restricted to acid and metal-complex dyes.

The time-consuming and relatively expensive full back-tanning process can be substituted by a simpler after-treatment using synthetic tanning agents or *syntans*. These are essentially based on sulphonated phenol-formaldehyde condensation products, which are water-soluble, anionic in nature and substantive to nylon under acidic conditions. Little published work concerning the composition of syntans is available. Kelson and Holt (1992), using high-performance liquid chromatography (HPLC), showed the diverse composition of syntans. Tomita and Tokitadaki (1980) showed that they consist of water-soluble anionic formaldehyde polycondensates of arylsulphonates and sulphonates of dihydroxydiaryl sulphones. Matexil FA-SNX (ICI) was described as a sulphonated product based on phenol sulphone.

Although less effective than full back-tanning treatment, the products improve the washing-fastness of nylon dyed with most anionic dyes. With careful selection of dyes, good fastness can be attained even in heavy depths. The washing fastness is reduced during subsequent dry-heat or steam-setting treatment, but the drop is less significant in case of syntans as compared to that during full back-tanning treatment. Syntan-treated materials exhibit slightly lower light-fastness. Most syntans are applied to the dyed and rinsed material in the presence of formic or acetic acid (pH 3.0–5.0). For example, the dyed material may be treated at 60–70°C for 20–30 min with 3–5% (o.w.m.) Nylofixan PI liq. (Clariant) and 1–2% (o.w.m.) formic acid (85%), followed by rinsing and drying.

Stripping of dyes

In some cases, it may be necessary to correct unlevel or excessively heavy dye-lots and redye to the original shade. Before stripping, syntan-treated material is to be treated for 30–45 min at 85°C in 2 g/L caustic soda (4 g/L for full back-tanned) and 1 g/L a non-ionic auxiliary. The treatment not only removes the tanning agent, but also reduces depth sufficiently to allow redyeing without chemical stripping.

Partial stripping is possible by treating with 20–30 mL/L ammonia, 1–2 g/L anionic wetting agent at boil for 30–45 min. A treatment with 10–20 g/L sodium hydrosulphite at 70°C prior to ammonia treatment is helpful in complete stripping. Stripping is also possible by treating with a suitable auxiliary (cationic or amphoteric auxiliary or a non-ionic vinyl polymer) adjusted to pH 9.0–11.0 at as high a temperature as possible for about 60 min.

For gross unlevelness, it is necessary to strip the fabric chemically in a fresh bath containing stabilised hydrosulphite, acetic acid and a weakly

cationic auxiliary. This is followed by rinsing and redyeing. Oxidative stripping (such as acidified sodium chlorite) is avoided due to degradation of the fibre and less colour build-up in redyeing.

2.12 Reactive dyes on nylon

Reactive dyes have potential interest for dyeing nylon due to their brightness and high wet-fastness properties. Some of the reactive dyes developed for cellulosic and wool fibres can be applied at boil on both nylon 6 and nylon 6,6 under weakly acidic conditions (pH 4.0–6.0). The covalent bonds form between the dye and amino end-groups, without an alkaline fixation step (Collishaw *et al.*, 1998). Dyeing nylon with reactive dyes leads to lower fixation levels in medium to deep shades than similar dyeing produced on wool. This problem stems from a paucity of nucleophilic end-of-chain amino groups. The average amino group content of nylon 6,6 is about 0.036 moles/kg of fibre. The dyes that contain an activated double bond and that react by a nucleophilic addition mechanism are capable of double addition at the end-of-chain amino group ($\text{-NH}_2 + \text{D-} \rightarrow \text{-NHD-} + \text{D-} \rightarrow \text{-N(D-)D-}$). Double addition means that the maximum depth achievable with a mono-functional vinyl sulphone dye of molecular mass 500 is 3.6% (o.w.m.) pure dye. In practice, lower values will be recorded due to the build-up of negative charge from the sulphonate groups on the fixed dye molecules, giving rise to strong electrostatic repulsion effects. Development of disperse vinyl sulphone reactive dyes and cationic vinyl sulphone dyes will thus be worthwhile. Other common reactive dye systems based on halogenated nitrogen heterocycles, for instance, Monochlorotriazine (MCT) do not give even moderate build-up since they are capable of only single reaction with a primary amine group. An MCT dye with molecular mass 500 will maximally give a fixed dyeing of 1.8% (o.w.m.) pure dye; the actual amount will be much less for the reason mentioned above (Lewis, 1998).

Mono-functional reactive dyes can be exhausted to nylon in medium and heavy depth, but only a portion of the total dye exhausted forms covalent bonds, the remaining portion is held by ionic bonds and van der Waal forces. The dyes exhibit excellent wet-fastness up to 0.7–1.0% (o.w.m.) for regular nylon, which is the limit for their reaction. The limit depends on the number and accessibility of free amine end-groups in the substrate and will obviously be higher for deep and ultra-deep nylons. When the concentration of dye exceeds the reaction limit, wet-fastness will be dependent on the molecular weight and substituent groups in the dye molecule. Below reaction limit, they are very susceptible to variations of amine groups. The coverage improves at higher depth. The coverage of physical variation is generally quite good. A wide range of mono-functional reactive

dyes is available, but the dyes are to be carefully selected to achieve good wash- and light-fastness.

Bi-functional reactive dyes are of considerable potential interest for nylon. The reaction limit is higher and is about 2% (o.w.m.) on regular nylon. Hence, medium to heavy shades can be produced, with all the dyes covalently linked to amine end-groups. These dyes can also be applied under weakly acidic conditions without an alkaline fixing treatment, when very high fastness to washing can be attended. Heavy depths can be achieved on deep and ultra deep-dyeing nylons. While good fastness to washing can be achieved with these dyes, it is more difficult to achieve good fastness to light on regular nylon.

In spite of the fact that bright and wash-fast shades can be achieved with reactive dyes, they are not widely used because of the following reasons:

- (a) Poor migration properties, when applied below their reaction limits.
- (b) High sensitivity to chemical variations in the substrate.
- (c) Difficulty in correcting or stripping a faulty dyeing.

Because of the above problems, reactive dyes, particularly bi-functional types, are to be very carefully applied. Though stripping may be possible by breaking the azo groups or the covalent bonds, the residual portions of the dye remain fixed with the amine groups. Consequently, it is difficult to redye the stripped material further with reactive or acid dyes. Obviously, redyeing may be done with disperse dyes, the substantivity of which does not depend on the available amine groups, but the wash-fastness will be poor.

Nevertheless, selected reactive dyes can be successfully applied on nylon. For mono-functional dyes, dye concentration may be exceeded by the reaction limit, but high fastness in those cases can only be achieved by after-treating with selected synthetic tanning agents. With bi-functional dyes, no dye will be taken up above reaction limit. Clearing treatment removes unfixed dyes and results in high wet-fastness.

The general method of dyeing nylon with reactive dyes is to set the dye-bath with:

- $x\%$ (o.w.m.) reactive dye
- 3% (o.w.m.) acid-liberating salt (ammonium acetate)
- 1 g/L weakly cationic levelling agent.

The liquor or material is circulated at 40°C for 10 min, the temperature is raised at the rate of 1°C/min up to boil, and the dyeing is continued for 1 h. For medium and heavy shades, the pH is to be lowered to about 4.0 for adequate exhaustion. When desired depth is achieved, the liquor is slowly cooled and the goods are thoroughly rinsed, hydro-extracted and dried. For

bi-functional dyes, it is advantageous to after-scour the dyed material at 60°C for 20 min.

Procinyl (ICI) reactive-disperse dyes can be applied under neutral or alkaline conditions, when dyes can form covalent bonds with the amine or amide groups of the fibre.

The dyebath is set at 40°C with 1 g/L non-ionic auxiliary and 2 g/L acetic acid (30%) to bring a pH 3.5–4.0. The previously dispersed and sieved Procinyl dyes are added and the material is run for 5–10 min. The temperature is raised at the rate of 1°C/min up to boil and the dyeing is continued for 30 min. Up to this stage, the dyes behave like normal disperse dyes and give very level dyeing. Then the dye liquor is made alkaline with soda ash to bring pH to 10–10.5 when the fixation is initiated. The dyeing is continued at boil for a further 45–60 min. Once the desired colour is attained, the goods are rinsed and soaped with 2 g/L non-ionic detergent and 2 g/L soda ash at 65°C for 20 min. After final rinsing, the material is dried.

Under atmospheric dyeing conditions, the reaction limit of Procinyl dyes is low. Consequently, the wet-fastness in heavy depths is largely dependent on the fastness of the unreacted dyes. Procinyl dyes can also be dyed at 100–120°C, when dye fixation occurs at any pH. However, for better leveling, the dye should be initially exhausted below 100°C.

The dyes in Procinyl range are compatible. On nylon, they produce shades having moderate to good fastness to light, good sublimation fastness and depending on depth, good fastness to washing. The shades are stable and fixation increases under the high-temperature conditions of heat-setting (Gulrajani, 1974b).

2.13 Dyeing of modified nylons

A number of modifications in the nylon have been made in order to alter its dyeability. Deep-dyeing nylons are produced in which the number of amine end-groups is significantly increased over that of regular nylon by introducing products like *N*-(2-aminoethyl) piperazine, phenylphosphonic acid derivatives or *p*-toluene sulphonic acid derivatives. In due course, ultra deep-dyeing polymers are produced by further increasing the ratio of amine to carboxyl acid end-groups. Tone-in-tone, reserve or cross-dyed effects can be achieved on a mixture of regular and deep-dyeing (or ultra-deep) nylons by dyeing with selected anionic dyes under controlled conditions. Another modification is to decrease the number of amine end-groups in the fibre in order to decrease affinity for anionic dyes by introducing groups like carboxylic, sulphonic or typically sulpho-isophthalic groups. This also increases the affinity of the fibre for cationic dyes. The so-called ‘basic-dyeable nylon’ is particularly prone to oxidative degradation. Oxidative bleaches should be avoided and it is advisable to add a small amount of antioxidant while

treating it above boil. It can be mixed with regular nylon to produce contrast effect by simultaneous dyeing with anionic and cationic dyes. Reserve effects can be achieved by using a single class of dye. Multiple colour effects can be achieved in fabrics made of mixtures of regular, deep-dyeing and basic-dyeing nylons. However, during production of these fibres, fugitive tints are to be applied in order to distinguish the colours.

For the production of differentially dyeable nylons, an important criterion is to have an optimum balance between the number of anionic groups ($-\text{SO}_3\text{H}$, $-\text{COOH}$) and end amine groups. It has been observed that fibres containing about 0.06 to 0.1 eq/kg of anionic groups have good affinity for cationic dyes. If the amount is less than 0.06, the affinity will be poor, whereas above 0.1 streaky dyeing will result. For deep-dyeing with cationic dyes and negligible staining with anionic dyes, the optimum anionic group and amine group contents should be about 0.07 and 0.02 eq/kg, respectively. The amine group content of about 0.075 eq/kg gives deep-dyeing nylon, while fibres with 0.05 eq/kg of anionic groups and 0.045 eq/kg of amino groups have almost equal affinity for cationic and acid dyes (Gulrajani, 1974a).

The dyeing characteristics of various differential-dyeing nylons can be listed as follows:

- (a) Regular-dyeing or normal nylon – normal affinity for anionic dyes and little or no affinity for cationic dyes.
- (b) Low-dyeing nylon – very low affinity for anionic and no affinity for cationic dyes.
- (c) Deep-dyeing nylon – high affinity for anionic dyes and no affinity for cationic dyes.
- (d) Ultra deep-dyeing nylon – very high affinity for anionic dyes and no affinity for cationic dyes.
- (e) Basic-dyeable nylon – little or no affinity for anionic dyes and high affinity for cationic dyes.

Anionic dyes reserve basic-dyeable nylon and give three tone effects on three acid-dyeable nylons, whereas cationic dyes reserve all but basic-dyeable nylon. Disperse dyes have approximately equal substantivity for all types of nylons.

There is a risk of complex formation and precipitation when anionic and cationic dyes are present simultaneously in the dyebath. Hence, blends of differential-dyeing nylons may be dyed by a two-bath or two-stage process, when the dyes of two dye classes are added separately. However, the process is uneconomical and usually an auxiliary (either non-ionic or amphoteric) called ‘anti-precipitant’ is added for simultaneous application of acid and basic dyes. Some commercial anti-precipitants are Alkanol CNR (Dupont), Lyogene MS (Clariant), Dispersol CWL and VL (ICI).

Cationic dyes selected for the purpose should give minimum staining on the deep- and regular-dyeing nylons.

For dyeing fabrics containing regular-dyeing, deep-dyeing and basic-dyeable nylons, first the tints are removed with 1–2 g/L sodium hydrosulphite at 80°C for 20 min and scoured, if necessary. The material is rinsed and entered in a dyebath containing:

- x g/L anionic dye
- 0.2 g/L antioxidant
- 1 g/L anti-precipitant.

(Thiourea is generally recommended as antioxidant, but recently it is claimed to be carcinogenic.)

Required amount of mixture (1:1) monosodium phosphate and disodium phosphate is added to bring pH to 5.0. The liquor or material is circulated and the temperature is raised to 50°C.

The required amount of pre-dissolved cationic dye is added. The temperature is raised to boil over 30 min and the dyeing is continued at boil. For addition of dyes, the temperature should be lowered to 80°C and anionic and cationic dyes are to be added separately. The temperature is then again raised to boil. The material is cooled and rinsed. The wet-fastness can be improved by syntan or full back-tanning treatment.

2.14 Dyeing of aramid fibres

Aramid fibres, aromatic polyamides, were first introduced in commercial applications in the early 1960s by Dupont under the trade name Nomex. The fibre is characterised by its excellent resistance to heat. The aramid fibres are almost undyeable with existing classes of dyes under ordinary conditions due to high degree of macromolecular organisation in the polymer chains, high crystallinity and high density.

Some authors propose modifying the surface of the aramid fibre by a suitable treatment such as a plasma treatment, so as to generate activation sites, where the dyes will then be capable of bonding. However, this type of treatment degrades the mechanical properties of the fibres, which is hardly beneficial when these fibres are intended to be used in fields requiring excellent properties in terms of resistance to fire and chemical products.

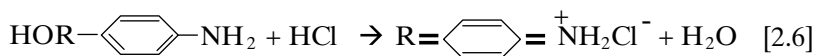
To overcome the difficulty in dyeing of aramid fibres complicated exhaustion procedures are used employing a strong polar solvent (swelling agent), creating voids in the fibre structure and then introducing a substance capable of forming a chemical bond with the dye in the swollen fibre. In most of the proposed methods, aramid fibre is pre-treated with an organic polar solvent, heated in an organic solvent to reversibly loosen its structure and

then a dye with active groups is incorporated into the structure. However, the solvent may create a pollution problem (Han and Jaung, 2009). The chosen solvent may be benzyl alcohol, cyclohexanone, dimethylformamide, dimethylacetamide, dimethyl-sulfoxide, acetophenone, benzaldehyde and mixtures thereof.

2.15 Basic or cationic dyes

The first synthetic dye, Perkin's Mauve belongs to basic or cationic dye class. Magenta and Malachite Green are also amongst the earliest synthetic dyes.

The basic dyes are so-named because they are derived from organic bases. They are also called cationic dyes as they ionise in water producing coloured cations. They are capable of salt-formation as shown in Equation [2.6].



The base, containing no chromophore, is colourless and the colour appears only on salt-formation. Cationic dyes are generally sold in salt form, usually chlorides, but sometimes as oxalates or even double salts with zinc chloride.

The outstanding characteristics of basic dyes are the brilliance and intensity of colour. The clarity of hue obtained with some basic dyes cannot be matched by any other dye class. Acid magenta, which is obtained by sulphonation of basic magenta, requires double the quantity of the latter to produce a full shade on wool. The basic dyes are not easily soluble in water and may form a sticky mass, which is difficult to bring into solution. Some of them are decomposed by boiling water and should be applied at temperatures of 60–65°C. They are readily soluble in alcohol or methylated spirit. With alkali, basic dyes are decomposed into colourless bases. Hard water or alkaline water should be avoided.

Basic dyes get precipitated, under certain conditions, when mixed with anionic dyes like direct or acid dyes. Consequently, they cannot be used together, except in the presence of anti-precipitants or at low concentrations. The conventional basic dyes have poor light-fastness and poor to moderate washing-fastness on wool and silk. Modified basic dyes with improved light-fastness are now widely used for acrylics.

The conventional basic dyes belong to several chemical classes, such as:

- (a) Diphenylmethane or ketone imine (presence of C=NH group), e.g. C.I. Basic Yellow 1.
- (b) Triphenylmethane, e.g. C.I. Basic Green 4, C.I. Basic Blue 5 and C.I. Basic Violets 3 and 14.
- (c) Thiazine (nitrogen and sulphur atoms forming a ring with benzene carbons), e.g. C.I. Basic Blue 9 and C.I. Basic Green 5.

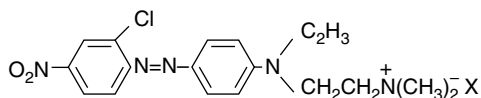
- (d) Oxazine, similar to thiazine, but nitrogen and oxygen atoms form a ring with benzene carbons, e.g. C.I. Basic Blue 12.
- (e) Azine, similar to thiazine, but two nitrogen atoms form a ring with benzene carbons, e.g. C.I. Basic Red 5.
- (f) Xanthene (two benzene rings linked by oxygen atom and methylene bridge) derivatives, e.g. C.I. Basic Violet 10.
- (g) Acridine (two benzene rings linked by a nitrogen atom and $-\text{CH}=\text{group}$) derivatives, e.g. C.I. Basic Orange 14.
- (h) Azo groups, e.g. C.I. Basic Brown 1.

The conventional basic dyes, mainly because of poor light-fastness, have virtually fallen into disuse on natural fibres. With the invention of polyacrylonitrile (PAN) fibres, difficulty in dyeing was encountered due to the very compact structure of the fibre. Fortunately, a number of modified varieties of the fibre were commercialised on which cationic dyes are substantive. Moreover, the basic dyes showed much better fastness on these hydrophobic fibres as compared to those on natural wool and silk. The photo-fading of dyes is faster in the presence of water and oxygen, which cannot gain access in the hydrophobic PAN fibres.

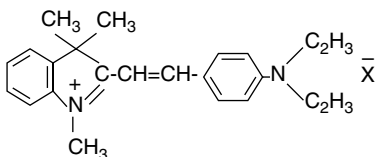
The improvements in dye structure of conventional basic dyes lead to modified basic dyes having higher light-fastness. They belong to three classes:

- (a) Cationic dyes containing a pendent cation with a non-resonating positive charge as in C.I. Basic Blue 49 and C.I. Basic Red 18 (Fig. 2.7).
- (b) Cationic dyes with a delocalised positive charge as in C.I. Basic Violet 7 (Fig. 2.8) and C.I. Basic Blue 5.
- (c) Cationic dyes with a heterocyclic ring containing a quaternary nitrogen atom, which does not form an integral part of chromogen as in Fig. 2.9.

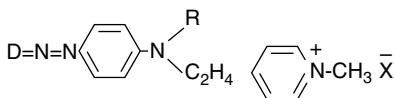
In addition to efforts to improve light-fastness, particularly important work has been done relating to production of dyes having specific affinity for acrylic fibres. Above a certain minimum concentration of dye in the liquor, the rate of adsorption, dc/dt , is, to a first approximation, proportional to the rate of diffusion of the dye into the fibre and can well be considerably higher with dyes that have a high compatibility (K value) than those that have a lower value. However, it is not the rate of adsorption that is the decisive factor for compatibility, but the combined effect of affinity and rate of diffusion. The physical significance of affinity is that the hydrophilic substituents will increase the affinity of dye towards water or dye liquor, or conversely decrease its affinity for hydrophobic fibres. On the other hand, hydrophobic substituents increase the affinity of the dye for acrylic fibres and reduce its affinity for water. Very bulky hydrophobic substituents



2.7 C.I. Basic Red 18.



2.8 C.I. Basic Violet 7.



2.9 Non-chromophoric heterocyclic ring with quaternary nitrogen.

can restrict diffusion of the dye and the two effects may cancel each other (Mayer and Siepmann, 1974).

Some of the ranges of cationic dyes manufactured for acrylic fibres by various manufacturers are Maxilon (Ciba), Astrazon (DyStar), Sevron (CKC), Yoracryl (YCL) and Sandocryl B (Clariant).

The normal basic dyes exhibit low migrating power on PAN fibres, which results in unlevel dyeing. 'Migrating cationic dyes' were synthesised to overcome the levelling problem. Work was essentially concentrated on hydrophilic dyes of large molecules and dyes of small molecular size. The introduction of hydrophilic groups lowers affinity of basic dyes to acrylic fibres, improving migration properties. However, the gain in migration is remarkably low, the degree of exhaustion decreases and the dyeing equilibrium is shifted in favour of the dyebath.

The large molecules (roughly dye cation, $I^+ > 450$) diffuse slowly and a slow rate of uptake favours level dyeing. Some commercial dye ranges have been developed with larger dye molecules. Although the rate of uptake matters, the temperature dependence of dye uptake is more important, which is at least as high with large molecules as with small. A disadvantage of using large molecules is that a long time is required to produce deep dyeing. On the other hand, the rate of exhaustion is too rapid in pale dyeing. As a whole, there is no appreciable advantage of larger molecules compared to conventional dyes.

The better migration properties of small molecular dyes in both natural- and synthetic-polymer fibres has been known for a long time. Small molecular Calcozine basic dyes were developed by Cyanamid in 1957–1958. In spite of good migration properties, these dyes failed to get established. Migration, at that time, was regarded as impossible for realisation in the dyeing of acrylic fibres with basic dyes.

Maxilon M dyes (Ciba), launched in 1975, disproved the old belief that the small molecules of dye will invariably result in poor wet-fastness. The glass transition temperature, T_g , of acrylic is above 100°C in dry state and around 70°C in wet state. The dyeing is carried out above T_g . In household laundering of acrylic material, the temperature is kept below 70°C to avoid fabric deformation. If this precaution is observed, the dye stays locked inside the fibre and good fastness is shown, even by dyes of small molecular size. Later, Hoechst launched Remacryl E and BASF launched Basacryl MX migrating cationic dyes.

However, with decreasing ionic weight, it becomes harder to meet pre-determined product requirements. The smaller the resonance system, it is more difficult to produce a blue dye or a dye with adequate intensity of colour, adequate light-fastness or good stability to hydrolysis. The difficulties in obtaining suitable small molecular dyes is apparent from the fact that out of 1000 such dyes tested in Ciba-Geigy laboratory, only five met the desired product requirements (Biedermann, 1979).

Any dividing line between non-migrating (NM) and migrating (M) types of dyes is purely arbitrary and makes sense only with respect to practical needs. The name 'M' dyes is therefore reserved for products that fulfil given minimum requirements.

Migration M% (i.e. levelness) can be expressed as follows in Equation [2.7]:

$$M\% = \text{amount migrated after time } t / \text{amount migrated after time } \infty \times 100 \quad [2.7]$$

For usual measurement, $t = 60$ (min).

Experience has shown that under standard conditions and given adequate circulation, the whole migration process over a prolonged period can be described in Equation [2.8]:

$$M\% = \tan \gamma \sqrt{t} \quad [2.8]$$

The term $\tan \gamma$ represents the slope of the migration curve plotted against \sqrt{t} . This is, however, an approximation, since with increasing \sqrt{t} , M tends to assume infinite value. The $\tan \gamma$ is termed 'migration value' for a given fibre, temperature and sodium ion concentration. It is also termed 'rate of

migration', actually representing rate of equalising or levelling. It is largely independent of concentration.

When applying conventional and migrating dyes to Orlon 72 at 100°C in the presence of 0.01 M Na⁺ and measuring the time in seconds, the following dividing line may be drawn (Biedermann, 1979):

	Tan γ	%M (1 h)
Conventional dyes (NM)	<1.1	<65
Migrating dyes (M)	>1.1	>65

2.16 Dyeing of acrylic fibres with basic dyes

Acrylic fibre has become the third largest produced synthetic fibre in the world. The production of acrylic fibres considerably exceeds the production of modacrylic fibres and the annual production in 1981 was 4627 million pounds (Holmes, 1983).

Regular acrylic fibres are produced from polymers containing 85% or more of acrylonitrile monomer, the other co-monomers usually being methacrylic acid, methylmethacrylate, vinyl acetate or a similar vinyl compound which are incorporated in order to improve dyeability and mechanical properties. They bring about a decrease in glass transition temperature enabling dyeing at lower temperature. In modacrylics, the acrylonitrile content is less than 85%. Acrylic fibres vary widely in their dyeability because of the different amounts of different co-monomers used with polyacrylonitrile that modify the fibre glass transition temperature ranging from 70 to 95°C according to the source of the acrylic fibre manufacturer.

Kidney or dog-bone shaped dry-spun fibres have better cover, good lustre, softer handle and better soil-hiding capacity. But due to limited internal surface, dye uptake is low. Micro-voids produced in wet spinning are considered to be an important factor for its better dyeability. Significant differences in dyeability occur between the dry- and wet-spun fibres as the surface area is in the range of 200–300 m²/g for wet-spun fibres, whereas that for dry-spun is less than 1 m²/g (Holmes, 1983).

Acrylic fibres can be dyed with cationic dyes only above the glass transition temperature T_g, which has a characteristic value for each type of fibre and for most fibres it lies between 70 and 80°C. Cationic dyes form a heteropolar bond with anionic groups of the fibre. The number of anionic sites in the fibre determines the saturation value, *S_f*, i.e. the maximum amount of dye which can be taken up by the fibre. Commercial acrylic fibres contain acidic sites to the extent of 30–35 milli eq/kg which impart dyeability with cationic dyes. The dye sites may be sulphonic or carboxylic groups; the dyeing behaviour in the latter case strongly depends upon the pH.

PAN fibres are hydrophobic and, therefore, do not as a rule possess marked affinity for water-soluble dyes, although there are exceptions. The fibres can be dyed with disperse dyes at 95–100°C, but the exhaustion is slow and build-up is not good for heavier shades. The saturation values are much lower and only pale to medium shades can be obtained. Better exhaustion can be obtained at high temperature, but above 110°C there will be excessive shrinkage of the fibres. Because of lower substantivity, disperse dyes can give level dyeing of good wet- and light-fastness. However, as penetration is poor, only low-molecular-weight dyes can be used, which have poor sublimation fastness causing staining of adjacent fabrics during pleating and hot-pressing. In heavier shades, the rubbing fastness may not be very good. The fibres get yellowed on boiling under alkaline conditions. The pH should be acidic during dyeing. The dyeing with disperse dyes may be carried out in a liquor containing 1 g/L sodium dihydrogen phosphate or 0.5 mg/L acetic acid (80%) together with 1 g/L non-ionic dispersing agent at boil for 90 min.

Dyeing of acrylic fibre is performed mainly by exhaustion processes (batch-wise). Another dyeing method with increased importance is the gel dyeing process. Dyeing in the gel state takes place during production of the fibre, i.e. after the fibre has been extruded and the solvent has been washed out. However, continuous dyeing of stock, cable and tops is also possible according to the pad steam process, before the fibre is stretched and dried.

2.16.1 Gel dyeing of acrylic fibres

For wet-spun acrylic fibres, the manufacture of producer-dyed fibres involves the passage of acrylic tow in the gel state through a bath containing basic dyes. PAN fibre is commonly wet spun from aqueous solutions of solvents such as sodium thiocyanate or DMF, the residual solvent being removed from the extruded filaments by washing. In gel dyeing, the washed filaments are passed, commonly in the form of tow, through an aqueous cationic or disperse dyebath followed by rinsing to remove surplus dye, drawing and finally drying. In gel state the fibre is highly absorbent and dye diffusion within water-filled voids of the substrate is rapid even at low temperature. The gel dyeing process is highly flexible. Small batches can be dyed economically – it is easy to change the dyeing shade. This is utilised in the Courtelle Neochrome process (formerly Courtaulds, now Acordis) to produce dyed acrylic fibres from a continuous fibre production line typically at a speed of 50 m/min with economic batch weights per colour of 250–500 kg. The technique has also been applied to dry-spun PAN fibres and drawing is done before dyeing (Holmes, 2000).

The liquid basic dyes are metered in at a rate appropriate to the acrylic tow mass and speed, the recipe being based on a computerised colour-match

prediction system allowing the selection of a very wide range of colours using a choice of the technically best dyes (i.e. easiest to apply and highest colour-fastness), or lowest cost dyes, or dyes least likely to cause metamerism. As the freshly coagulated acrylic tow passes through the dyebath, the basic dyes diffuse inside the gel state acrylic tow in a matter of seconds. The dyed tow is then drawn and steamed, crimped and cut to the appropriate staple length for use in technical textiles, or may be used alternatively in filament form.

Acrylic fibres are very delicate and are in semi-plastic state at boil. The material should be cooled very slowly till the temperature falls below 75°C and the movement of the material should be maintained during the time in order to prevent the formation of permanent creases and distortion. Residual dye in the dyebath, if any, may be deposited on the material during cooling, which can be removed by boiling with 1 g/L acetic acid and 1 g/L emulsifier.

The features of gel dyeing are summarised below:

- (a) Production of any hue, from pale to deep, is possible (only with cationic dyestuff)
- (b) Production possible from a minimum of 5 tons
- (c) Quick colour switching
- (d) Costs one tenth to one-fifth of tow dyeing
- (e) Environment-friendly as it uses little water.

2.16.2 Principle of acrylic dyeing

Fundamentally, there are two ways to achieve level dyeing, namely:

1. Controlled, level uptake is ensured from the start of dyeing so that subsequent correction is unnecessary.
2. Uncontrolled uptake, i.e. uptake accompanied by a greater or lesser degree of unevenness, is allowed, followed by a migration stage in which the unevenness is corrected.

This classification is valid for all fibres and dye classes. Due to their non-migrating nature, conventional basic dyes for acrylic fibres have to be applied by a closely controlled exhaust process (method 1). The factors affecting the rate of uptake of basic dyes on acrylic fibres have long been recognised and the recommendations for controlling dye uptake are:

- (a) Careful control of temperature
- (b) Use of compatible dyes
- (c) Appropriate addition of retarders.

The temperature has a marked effect on dye uptake of acrylic fibres as compared to other fibres. Another important aspect, relating especially to pale dyeing, is that even in the cold, an appreciable amount of dye is unevenly adsorbed by ion exchange on the fibre surface, which is almost impossible to correct later. Over the years, efforts have been made to optimise the dyeing process for acrylics by controlling dye uptake. Both the fibres and the basic dyes were characterised by several technical parameters and the dyeing procedures have been refined based on such knowledge.

For better levelling, migration, i.e. mobility of the dye within the fibre, can be increased by raising the temperature to about 120°C, but damage to the fibre is inevitable. Secondly, the glass transition temperature of the fibre can be reduced by using carriers. Neither of the two proposals has been accepted commercially. A quite different idea was to add cations of low ionic weight such as Na^+ , $\text{N}(\text{CH}_3)_4^+$ and small molecular cationic retarders in the dyebath. Migration promoters such as these are intended to displace the dye from the dye sites, thus promoting desorption and migration.

Two models, the Langmuir isotherm and Donnan equilibrium, have been used to describe cationic dyeing as a cation-exchange process. The Langmuir isotherm treats all anionic sites in the fibre as identical and includes all influences of dyeing additives such as electrolytes in one constant (Guion and McGregor, 1974). A constant partition ratio for modifying the Langmuir model has been used to explain excess dye adsorption by anionic sites in the fibres (Takahashi *et al.*, 1964). The Donnan approach separates the acrylic fibre sorption sites into weak and strong anionic groups and considers the influences of dyebath additives separately, enabling it to predict individual influences of pH, salts and fibre structure on dye sorption.

The theory of dyeing acrylic and modacrylic has been discussed exhaustively by Beckmann (1969). Dyeing with cationic dyes occurs by an ion exchange mechanism or a simple ion distribution. The three steps involved in dyeing are:

- (a) Adsorption of dye cations at the fibre surface
- (b) Diffusion into the fibre
- (c) Occupying dye sites within the fibre.

The first two steps determine the rate of dyeing, while the last influences the dyeing equilibrium. Adsorption of cationic dyes on the surface of acrylic fibres can be described by a Langmuir isotherm with saturation occurring at low concentrations of dye in the bath. Within the range of concentration

used in practice, the fibre surface is saturated with dye. The rate of dyeing is almost independent of liquor ratio.

During dyeing, sodium or hydrogen ions originally present in the fibre are replaced by dye cations. At equilibrium, the dye concentrations, C_F in the fibre and C_S in the dyebath, closely follow a Langmuir isotherm with pronounced saturation and high affinity. The maximum number of dye cations that can be taken up is equal to the number of accessible anionic dye sites in the fibre. This stoichiometric relationship enables the status of the dye-fibre system, relative to saturation, to be calculated. Some constants, characteristics of dyes and fibres, have been introduced. The Society of Dyers and Colourists defined the following dyeing parameters:

‘Fibre saturation value, A' , representing the number of dye sites available in the fibre, as that quantity (on % fibre weight) of pure hypothetical dye of molecular weight 400 which gives 90% exhaustion of the original dyebath when applied for 4 h at 100°C at M:L ratio of 1:100 and at pH 4.5.

‘Fibre saturation value, S_F ’ is defined as quantity of dye in the fibre and not at the starting dyebath and as such, $A = 1.1 S_F$.

‘Dye saturation factor, f ’, transforms quantities p of commercial dyes (in % fibre weight) into molar units of ‘ A ’, i.e. equimolecular quantity of pure hypothetical dye of molecular weight 400. f decreases for a given dye as the diluent-content increases.

$$\text{At saturation, } p_{\text{sat}} \times f = A \quad [2.9]$$

If $p \times f > A$, the surplus dye ($p - p_{\text{sat}}$) will remain in the dyebath.

If $p \times f < A$, then at equilibrium, almost all dye in the system will be taken up by the fibre. For a combination of dyes, the equation becomes,

$$p_1 \times f + p_2 \times f + \dots < A \quad \text{or} \quad \sum p \times f < A \quad [2.10]$$

Cationic retarders having affinity similar to those of the dyes are included in the term $\sum p \times f$.

These conditions are independent of the material:liquor ratio within practical range of 1:10–1:40. The dyeing temperature does not affect equilibrium exhaustion appreciably since the range of maximum temperatures used is narrow, the affinities are high and heats of dyeing are normal, and ‘ A ’ does not depend significantly on temperature. For most acrylic fibres, ‘ A ’ increases slightly with increasing pH within the practical range, but the increase is significant only for fibres having weakly acidic (carboxylic) dye sites.

A quantity of practical significance, 'relative saturation value, S_{rel} ', is the ratio of the number of dye cations in the system and that of dye sites in the fibre as shown in Equation [2.11]

$$S_{\text{rel}} = \sum p \times f/A \quad [2.11]$$

If S_{rel} is kept constant and certain other conditions (like compatibility of dyes and retarders, control of temperature consistent with fibre dyeing rate constant) are maintained, the dyeing of different dyes on varying acrylic fibres will be similar. A higher value of S_{rel} leads to more level results, but according to the definition or Equation [2.10], the value of S_{rel} must be less than one for good equilibrium exhaustion. Therefore, S_{rel} should be balanced by using rapid-dyeing techniques or by careful controls on dyeing.

The safe levelness is obtained whenever the saturation of the fibre reaches a certain value, which depends on the working conditions. It was found that good results could be obtained with a relative saturation of about 0.9 when dyeing bulk yarns made from wet-spun fibres and 0.6–0.7 from Orlon 42 or Dralon. It follows that the relative saturation should be different, depending on the kind of fibres used. The important factors are 'fibre saturation value, S_{F} ' and the rate of dyeing (Beckmann, 1969). Different dyestuffs will require different 'relative saturation value, S_{rel} '. The required relative saturation is adjusted by adding an adequate amount of cationic retarder. High-affinity dyes with low migration capacity will require a higher relative saturation (meaning they need more retarder) than low-affinity dyes of marked migrating capacity under the influence of cationic retarders or electrolytes.

Affinity is important in relation to:

- (a) Equilibrium exhaustion when the amount of dye is near to or above the saturation limit.
- (b) Blocking effect in dyeing with a mixture of dyes.
- (c) The effects of electrolytes and retarders.
- (d) Migration and levelling properties.

A few dyes have been developed which have extremely low affinity and high diffusion coefficients. These dyes have better migration properties than those of normal cationic dyes as mono-sulphonated acid dyes on nylon.

As absolute affinity is difficult to measure, 'relative affinity A_{r} ' is determined from equilibrium exhaustion of the dye in presence of a standard dye or cationic auxiliary (colourless and does not interfere with photometric measurements) for which A_{r} has been assumed to be unity.

' A_{r} ' indicates migration power of the dye, the higher value meaning less migration. It is closely related to compatibility. Dyes of high A_{r} values are

less influenced by electrolytes, cationic retarders or other cationic dyes, and are more strongly influenced by anionic retarders than are dyes of lower A_r value. It appears that it has no relationship with the rate of dyeing. A_r values quoted by different manufacturers are based on different scales (e.g. logarithmic or linear) and different standards, and as such are not comparable.

The adsorption of individual cationic dyes is influenced by the presence of others in the dyebath. In mixed or compound shades, if all the dyes used exhaust at the same rate, the depth and not the hue changes with time. The dyes are said to be compatible in that particular combination under the above dyeing conditions. Since very little migration of cationic dyes occurs on acrylic fibre, the dyeing should be very level from the start. Any unlevelness must be corrected during the exhaustion stage. This is virtually impossible in case of combination of incompatible dyes. Combination of compatible dyes requires less dyeing time and less levelling agent thus assuring better reproducibility and levelling.

The cationic dyes may be characterised according to compatibility by a value called 'compatibility value K ' ranging from 5 (slow diffusing) down to 1 (rapid diffusing), which can be measured by a standard test method proposed by the SDC (1972). Dyes of equal K value are compatible in combination on each acrylic fibre under all practical exhaust dyeing conditions except in the presence of anionic dyes or auxiliaries.

Theoretically, K is determined by affinity and diffusion coefficient, the latter playing a minor role. In combinations, the dyes of lower K value will exhaust more rapidly. However, K does not itself indicate rate of dyeing. The actual rate of exhaustion of a dye depends on the presence of other dyes or retarder. A combination of dyes, all having $K = 5$, might exhaust more rapidly than the one in which all dyes have $K = 3$. The effect of cationic retarders and electrolytes is more pronounced with dyes of higher K value, because K is determined mainly by affinity.

Electrostatic attraction is not the only major interaction that occurs between cationic dyes and acrylic fibre. Hydrophobic interaction also plays an important part in dye/fibre affinity. Salt anions such as SO_4^- and H_2PO_4^- can increase hydrophobic interaction between the dye and the fibre and thus increase dye sorption (Yang and Ladisch, 1993). The dye distribution coefficient K_D in the Donnan approach cannot be treated as a constant. It is a function of chemical potential changes due to the hydrophobic interaction.

The investigations (Rohner and Zollinger, 1986) on dyeing kinetics of a cationic dye on two commercial acrylic fibres show that neither the pore model nor the free-volume model alone explains all aspects of the mechanism of dyeing acrylics with cationic dyes above the glass transition temperature of dyeing (TD). They postulated that pore diffusion and matrix diffusion are present simultaneously, but in varying ratios depending on the type of fibre.

2.16.3 Retarders

Cationic retarders are mostly quaternary amine compounds with long aliphatic chains and also aromatic groups, which determine their affinity. Some of the commercial cationic retarders are Levagal PAN (DyStar, formerly Bayer), Retargal AN (Clariant), Tinegal CRA (Ciba) and Basacryl Salt G (BASF). They form colourless cations in water, which compete with dye cations at the surface and inside the fibre. They replace some dye cations from the fibre surface reducing dye concentration gradient effective for diffusion. They also increase the total number of cations effective for relative saturation, S_{rel} . The effect of cationic retarders is, therefore, two-fold, in that they decrease the rate of exhaustion and increase S_{rel} value. Consequently levelness is improved, but there is a danger of over-saturation or blocking. The decrease in the rate of exhaustion can also be achieved by temperature control. However, the temperature influences the rate of dyeing by changing the diffusion coefficient, not the concentration gradient. The temperature also does not affect S_{rel} . The retarder does not affect diffusion coefficient. The difference between the effects of temperature and retarder is especially apparent in pale dyeing. The small amount of dye present in the dyebath can be fully accommodated on the fibre at the fibre surface. The adsorption is rapid and cannot be controlled by temperature. The unlevelness is almost certain, especially on poorly prepared material. This adsorption strike is more pronounced when the S_{rel} is lower. Thus, the addition of a cationic retarder will improve the situation.

The knowledge of saturation factor, f , is essential to prevent blocking. The quantity of retarder should be small enough to satisfy Equation [2.10]. Optimum exhaustion and levelling properties require the compatibility value K of the retarder to be about equal or slightly higher than that of the dye, because the retarder and dye should exhaust at the same rate.

In addition to the normal cationic retarders, Glauber's salt is often used as a weak, but inexpensive retarder or migration aid. Its effect is greater with dyes of higher K value. The concentration of Glauber's salt should be less than 2.5 g/L. It may adversely affect the action of other levelling agents. In a few cases, Glauber's salt gives a better levelling effect, but only at higher concentration (above 2.5 g/L) which is not recommended. Common salt may be used, but should be free from contaminants like iron. It may, however, corrode the dye vessel made of certain types of stainless steel.

The work showed that the nature of the cation caused a marked change in dyeing kinetics, whereas the anions of the electrolytes exert little influence. The retarding effect of various cations on the adsorption of purified C.I. Basic Red 29 followed the order given below (Holmes, 1983):



Both the dyeing rate and the equilibrium adsorption were found to be significantly affected, when the ionic volume is greater, but the effect of $(C_4H_9)_4NCl$ was noticeably higher than all others studied. It was suggested that the effect of the cation in modifying the physicochemical properties of the aqueous solutions and the water-structure breaking effect which increase with increasing radius of the cation from Li^+ to Cs^+ were important factors. The retarding effect produced by electrolytes was lower at higher dyeing temperature and this may reflect the lower hydration of the cation at high temperatures.

Low-affinity retarders usually have smaller molecules and do not show serious blocking. Their effect on migration is between that of sodium sulphate and cationic retarders having affinity similar to dyes, these are called migration aids. In addition to normal retarders, they can be used in larger quantities to affect migration. Due to low affinity (high K value), they exhaust after the dye and exert little influence in the exhaustion stage of dyeing. However, they can be applied prior to dye, when they can prevent excessive and uneven strike of the dye. They can also be used as a levelling agent during shading in order to match a shade.

Some retarders are unstable and slowly become ineffective during dyeing due to chemical reactions like hydrolysis of esters. They give less or no blocking and are recommended for use when shading at high temperature.

Cationic polymeric retarders with up to a few hundred cationic groups per molecule can be used for controlling the rate of dyeing. They give superior coverage of two components of varying dyeability in bicomponent fibres. Since they do not penetrate the fibre, they do not truly increase S_{rel} and have little or no positive effect on migration.

The main practical application for retarders in dyeing acrylics is to achieve level dyeing by reducing the effect of temperature and concentration differences in the bath; by lowering the dye rate there is more time for these differences to level out. In this respect, the polymeric retarders are superior to conventional retarders because they are effective in much lower concentration and remain effective throughout the dye cycle.

A second area where the new polymeric retarders have found practical use is in union dyeing of blends of fibres with different dye site content. In this situation, we make use of the selectivity of the polymeric retarder to reduce the dye rate of the fast dyeing component to approach that of the slow dyeing fibre so that an acceptable union results. For example, in skein dyeing blends of fast dyeing Type 21 and slow dyeing Type 42 'Orlon', conventional anionic or cationic retarders do not give an acceptable union. With a polymeric retarder, the shades of the component fibres are close enough for an optical union in blends. Polymeric retarder technology generally increases the number of combinations of heathers, tone-on-tone and union dyeing which can be achieved with fibre blends. In addition, fibre

combinations having desirable performance characteristics can now be more easily employed without adverse dye effects (Dullaghan and Ultee, 1973).

2.16.4 Methods of acrylic dyeing

The ionic attraction between basic dye and sulphonic acid dye site in acrylic fibre is strong, which yields high colour-fastness to washing. The close-packed physicochemical nature of acrylic fibres and the strong dye-fibre bonding can result in poor migration and levelling properties during dye application, but impart very high colour-fastness to light.

Cationic dyes show excellent build-up and fastness and many give brilliant shades on acrylics. They are usually less expensive than disperse dyes. However, their migration properties are, in general, poor. The dyeing should be carried out very carefully so that the dye uptake is uniform from the beginning. The effects of dyeing conditions should be known and are to be carefully controlled. Material to liquor ratio does not exert much influence.

The temperature range of dyeing should extend to about 30°C above T_g , i.e. between 75 and 105°C. Migration and levelness are better at higher temperature. But different acrylic fibres show varying degrees of mechanical instability at high temperature. There may be flattening of fibres resulting in loss of bulk and handle. Maximum permissible temperature depends on fibre type, physical variables like tension, package density, etc., and the characteristic of the dyeing machine.

The normal range of pH for dyeing of acrylic fibres is 3.5–6.0, in which both cationic and disperse dyes are very stable. At lower pH, levelling is better and for cationic dyes, the rate of dyeing and the equilibrium exhaustion are lower. Most acrylic fibres show an increase of 10–20% in fibre saturation value 'A' and rate of dyeing for one unit increase in pH within the said range. This can be utilised to cope with saturation problems, e.g. for very deep colours on fibres with low 'A' value or while shading or redyeing. The evaporation of acetic acid may not be of much problem, until pH increases above 6.0 when dyes become unstable. It is better to use an acetic acid–sodium acetate buffer system to maintain pH of 4.5–5.5. For deep-dyeing, pH may be higher and retarder is not used. Sulphuric acid (pH 2.0–3.5) is sometimes recommended for level-dyeing of wool–acrylic blends, but many cationic dyes are unstable in this pH range.

Addition of 0.5–2% (o.w.m.) (or higher amount for deeper shades) polyglycol type non-ionic detergent may be added in the dyebath to keep the dye vessel clean and after-scouring may not be necessary. This also prevents precipitation of dye due to anionic residues in the material. 0.1 g/L potassium dichromate may be added when reducing metal ions (Cu^+ , Fe^{++}) are present in water, if permissible from effluent point of view.

The dye is dissolved by pasting with equal quantity of acetic acid (30%) followed by addition of 20–50 times boiling water. Some dyes require special methods and some require warm water. A typical recipe for dyeing is as follows:

- $x\%$ cationic dye
- 1–2 g/L acetic acid (30%) to bring pH 3.5–4.0
- 0–2.5 g/L Glauber's salt or common salt
- 0.25–0.5% non-ionic detergent
- $y\%$ cationic retarder.

(All percentages are o.w.m.)

The value of y should be chosen according to depth of colour, the type of dyes and the fibre. Saturation should be avoided considering requirements expressed in Equation [2.10]. There is very little adsorption below 75°C and the critical temperature is 80–100°C. It is, therefore, advisable to raise the temperature rapidly to 75°C and then allow 1 h for the liquor to reach boil. The bath should be kept at the maximum temperature for 10–15 min after complete exhaustion (after there is no visible change in the colour of dye liquor) for sufficient penetration and to avoid ring dyeing.

When dyeing is carried out in an open vessel, the highest obtainable temperature should be maintained and the temperature should not be allowed to fall, because levelness of dyeing is very sensitive to temperature variations. The dyeing, if possible, may be carried out at 105–107°C because exhaustion is more rapid and the migration is better.

At boiling temperature there is very little migration. It is, therefore, of greatest importance that the adsorption by material should be uniform throughout the dye vessel and that the control is exercised over the critical temperature range. Because of poor migration properties, dyes of similar K values should be chosen in the mixture. Cooling after dyeing should be slow (about 1°C min) to avoid undesirable handle, crease marks, etc. especially in fabrics.

Well-exhausted dyeing requires only a brief rinse in water. Soaping may be necessary with some heavy depths and may be carried out at 60°C with soap and 1 g/L sodium hydrosulphite.

2.16.5 Constant temperature dyeing

The adsorption of cationic dyes is influenced by even a few degrees of difference of temperature. It was found that dyeing at constant temperature (85–90°C) would give rise to an adsorption curve with a gradual and uniform profile. The temperature chosen depends on the type and amount of dyes and retarders, and also on the fibre. It is to be carefully calculated using appropriate tables and charts. BASF recommended the 'Defitherm Process'. The main feature of the process is that the goods are dyed at a temperature,

which is defined by means of bath exhaustion time. A quaternary ammonium compound, Defithermol TR, is recommended as retarder-cum-thermo-regulator. Like cationic dyes, the compound has definite exhaustion on each type of acrylic fibre. The percentage of dye is expressed as equivalent to Defithermol TR and is called Defitherm Value. Normally dyeing is recommended to be carried out at a temperature, T_{60} , at which the bath exhausts in 60 min. The use of Defithermol TR is required only if the dyeing is carried out at a temperature higher than T_{60} . Defitherm Tables provide the following data:

- (a) Saturation values of various acrylic fibres.
- (b) Defithermol TR equivalent of cationic dyes.
- (c) Total % cationic product expressed as Defithermol TR by adding multiplication product of % dye and Defithermol TR equivalent of each dye in a combination.
- (d) Initial dyeing temperature, T_i .
- (e) Actual dyeing temperature, T_{60} on the basis of total % cationic product.

The dyebath is raised to the initial dyeing temperature, T_i , and pH is adjusted to 4.0–4.5 with acetic acid. The goods are entered and circulated for 15 min to wet out and to achieve uniform temperature. The temperature is rapidly raised to the desired dyeing temperature (T_{60} or higher) and circulated for 5 min. The previously dissolved dye and Defithermol TR are added in as highly concentrated form as possible. The bath is held at selected temperature ($\pm 1^\circ\text{C}$) until exhaustion is complete requiring about 60–90 min. If adsorption is incomplete, the temperature may be raised by 2–4°C for complete exhaustion. The shading dyes, if necessary, should be added without raising temperature. When the match is satisfactory, temperature is raised to boil over a period of 10–15 min, after which dyeing is continued for 20 min for complete fixation of dyes. During cooling, a pause of 15 min is given at the dyeing temperature followed by cooling to 60°C.

The advantage of this method is that temperature variations within the dyeing system, a major cause of unlevelness, are less likely to occur. There are two disadvantages. Firstly, the exhaustion curve at constant temperature has a shape, which may not be truly optimised. Secondly, the rate of dyeing strongly depends on temperature; constant temperatures are to be correctly calculated and maintained to within $\pm 0.5^\circ\text{C}$, which is difficult to achieve.

The difficulties can be partially overcome by approaching the constant dyeing temperature slowly. This is similar to stopping at a temperature below the maximum temperature.

In constant temperature dyeing methods, only a minimum amount of retarder is recommended to prevent excessive adsorption strike, to reduce

the cost of retarder. Here, dyeing is mostly regulated by temperature control and not by control of relative saturation, S_{rel} . There are great differences in S_{rel} values for pale and deep-dyeing. The probability of unevenness will vary and will be higher for pale dyeing.

2.16.6 Rapid-dyeing method

Several rapid-dyeing methods have been reported for acrylic fibres. Most of the methods are based on dyeing in optimised conditions achieving level dyeing from the start of the process, eliminating the need of time of migration or dead time prior to exhaustion stage. The rapid-dyeing method based on migration and use of migrating cationic dyes has also been proposed. The temperature control is simple – only the end temperature is controlled and not the rate of increase of temperature.

However, the degree of unlevelness introduced is unpredictable when the exhaustion is not controlled by temperature. Hence, actual migration time required is unknown and sufficient time must be given for the worst degree of unlevelness possible. The dyeing time will be longer than that for dyeing level from the beginning. During optimisation of the process, a few important points are to be considered such as:

- (a) The compatibility of dyes and retarders.
- (b) The amount of cationic retarder used should bring the relative saturation, S_{rel} , to a standard value, which may depend on the nature of the fibre and dyes, for each recipe.
- (c) The rise of temperature should be adjusted to give a steady and uniform increase of exhaustion with dyeing time. The optimum rate of dyeing depends on the machine (e.g. liquor flow) and the standard of levelness required for the goods. The rate of temperature rise is generally linear with time.

The Astrazon Rapid-Dyeing Method (Beckmann, 1969) was derived as follows. First, the relative saturation value, which gave the best results, was determined. Then the correct way of varying the temperature was calculated for the above relative saturation value and for the required rate of adsorption (considering necessary fibre and dyestuff data). From practical experience, the rate of adsorption should normally be selected in such a way that no more than 15–20% of the dyestuff should go on the fibre for every 10 min of dyeing time. If the dye goes on the fibre too quickly, there is a risk of unlevel dyeing. On the other hand, if the rate is too slow, there will be a certain amount of dead time. However, this is preferred by the dyers, because uneven dyeing is considered highly undesirable.

The best possible curve is approached by selecting the initial temperature properly (i.e. the temperature at which the dye has not gone into the fibre appreciably) and also the best possible way of increasing temperature. The temperature rise can always remain the same – approximately 1°C for every 2.5–3 min. However, it is necessary to determine the initial temperature for each dyeing. The following figures must be known to determine the optimum amount of retarder and the initial dyeing temperature:

Dyestuff data: concentration ($p\%$)
 combination index (K)
 saturation factor (f)

Fibre data: rate of dyeing (V)

Fibre saturation value (S_F).

Beckmann (1969) provides the necessary data for the above parameters in the form of five tables. Tables 2.1 and 2.2 of Beckmann (1969) provide Astrazon dyestuff data (f and K) and fibre data (V and S_F values of various commercial acrylic fibres), respectively. The individual dyestuff concentration value is determined from Table 2.3 of Beckmann (1969) for every dyestuff, using % depth ($p\%$) of each dye and f value for the particular dye. These concentration values for all dyes used in the combination shade are added to give the total dyestuff concentration value, R_F . It is a measure for the number of dyestuff cations, which occupy the fibre. The total concentration value R_G , is noted from Table 2.4 of Beckmann (1969) using fibre data namely S_F and V and dyestuff data, K . The initial dyeing temperature is noted from Table 2.5 of Beckmann (1969) for the total concentration value, R_G and for the V value of the fibre.

A large range of shades of high level of wet-fastness can be obtained with a three-colour combination of $K = 3$ dyes, namely:

- C.I. Basic Yellow 28
- C.I. Basic Red 46
- C.I. Basic Blue 41.

The dyes with $K = 1$ may be useful for low-affinity fibres and for production of dark shades. A wide gamut of shades can be obtained with trichromatic combination of $K = 1$ dyes, namely:

- C.I. Basic Orange 42
- C.I. Basic Red 45
- C.I. Basic Blue 69.

When high level of light-fastness is required, such as for furnishing fabrics or carpets, the following dyes can be used on dry-spun fibres to obtain

Table 2.4 General recommendations for acrylic dyeing

Dyebath additives	Light hues	Medium hues	Deep hues
Non-ionic dispersant, g/L	0.2–0.5	0.5	0.5
Acetic acid, final pH	3.6	3.6	4.5
Sodium acetate anhydrous, g/L			0.5
Sodium sulphate anhydrous, g/L	5	5	
Cationic retarder (K value of about 3) % o.w.m. depending on the quantities of dyes present in the recipe	1.5–3	0.3–1.5	
Dyeing parameters			
Starting temperature, °C	75	80	85
Final temperature, °C	95	98–100	98–100
Heating rate, start to end, usually linear, °C/min	0.5	0.3–0.4	0.25
Maximum hold time at 98°C, min	20	40	60
Maximum hold time at 102°C, min	15	30	40
Cooling after dyeing	0.3°C/min up to 60°C		

adequate light-fastness:

- C.I. Basic Yellows 28*, 63
- C.I. Basic Orange 28
- C.I. Basic Reds 18*, 24, 25, 78
- C.I. Basic Blues 45, 47*.

(The dyes with * may be used in mixture for black shade.)

The dyeing process of migrating cationic dyes (e.g. Maxilon M, Ciba-Geigy) can be broken down into an exhaustion phase followed by migration phase. It is not necessary to pay much attention to the exhaustion phase because any unevenness occurring can be corrected later. However, if major corrections are to be carried out, long migration times will be required.

The migrating cationic dyes must be compatible and are normally applied using electrolyte together with a migrating cationic retarder with a similar *K* value to that of dyes and a similar migration value ($\tan \gamma$). The use of conventional cationic dyes and retarders are not recommended to be used with migration cationic dyes. A general guidance on dyebath additions and parameters of acrylic dyeing are given in Table 2.4 (Hunger, 2003).

2.16.7 Stripping of cationic dyes

Depending on the dyes used, partial stripping, to remove about 30% of the dye present, can be achieved by treating the goods in a fresh boiling bath

containing either 1–10% (o.w.m.) anionic retarder and 1 g/L acetic acid (60%) or 1–5 g/L Marseilles soap.

High-temperature enhances stripping. The effect may vary for different dyes and, consequently, the hue of compound shade may change drastically. The treatment removes cationic retarder substantially and may therefore be used prior to redyeing.

Stripping may be carried out with oxidative bleaching agents, e.g. free chlorine or chlorine dioxide. Complete stripping is not possible with all dyes.

Some modacrylic fibres are prone to delustering during dyeing and may require relustering by boiling for 30 min in a high concentration of electrolyte (e.g. 50–200 g/L sodium chloride) or by dry-heat or treatment in saturated steam.

2.17 Dyeing of olefin fibres

Polyolefin (PP) fibres are defined as fibres spun from polymers or copolymers of ethylene and propylene. For textile applications only PP is successful to some extent. Coloration of polyolefins is difficult, because the homo-polymers are of very inactive nature and are virtually undyeable.

PP fibres are derived from an inexpensive raw material that produces fibres with a series of desirable properties such as dimensional stability, low weight, low water absorption, resistance to chemicals and rot-proof. Consisting of pure aliphatic hydrocarbons, these fibres have no groups that can interact with dyes normally used for textile dyeing.

Some of the earlier efforts made for coloration of these fibres are:

1. Surface oxidation of methyl to carboxylic groups. However, the method is not very successful.
2. Copolymerisation with other monomers having affinity for dyes. But the co-monomers inactivate Ziegler-Natta catalyst, which is used for manufacturing these stereo-regular polymers.
3. Grafting of dye on to the fibre.
4. Introduction of metal salts during spinning and subsequent dyeing with dyes able to complex with metal ions.

However, none of the methods described above is commercially successful. Hence, PP at present is almost fully (100%) mass coloured. While this has the benefit of very good colour-fastness, there are two significant disadvantages. The first is that introducing new colours involves a relatively complex colour matching step. Secondly, there is no scope for dyeing goods as per fashion trends. This means that relatively large lots of fibre are made for

every new colour, and the time required to implement a new colour concept to the final fabric or garment can be long.

Numerous attempts have been made to modify PP to make it dyeable from aqueous liquor. In one method, the PP structure is loosened by a polyether or a polyamide, making the fibre accessible to disperse dyes. Another recommends etching the fibre with a low-temperature plasma in the presence of O₂. The depth of shade and fastness properties of disperse dyes are sufficient for many textile purposes including floor coverings. In all dyeing processes, the low melting point of the PP fibre must be taken into account. The fibre becomes plastic at 130°C, and treatment temperatures must be kept below 120°C to avoid excessive shrinkage (Hunger, 2003).

FiberVisions (www.fibervisions.com) has developed a revolutionary new PP fibre, CoolVisions™, a dyeable PP fibre that meets the needs of facile dyeing and PP fibre characteristics by incorporating an additive within the PP fibre. The fibre can be dyed using conventional disperse dyes in a manner similar to that used for polyester fibres (TW Special Report, 2006).

Dyeable PP has remained a very important challenge to all the polymer and textile chemists for many decades. Approaches to dyeing PP using polyblends, copolymers, and plasma treatment have been all thoroughly explored. Currently available technology for the manufacture of dyeable PP relies mainly on copolymerisation, polyblending and grafting technologies. Examples are vinylpyridine/styrene copolymer or poly (ethylene/vinyl acetate) blended with PP for disperse dyeability; stearyl methacrylate, dimethylaminopropylacrylamide, or basic imidized styrene-maleic anhydride copolymer for acid and disperse dyeability; stearyl methacrylate-maleic anhydride for basic and disperse dyeability and organo-metal-complexes for specially selected dyes. The nanoparticles are introduced to the PP matrix in a melting or dissolving process with the help of heat and/or organic solvent and/or mechanical blending including the use of sonic and/or electric field. After being properly distributed into the polymer matrix, the nanoparticles are supposed to provide chemical and/or physical linkages to the dyes. In the case of nanoclays, it should carry or be able to develop charged groups or other functional groups that can attract dyes via chemical and/or physical linkages (NTC, 2002).

The various techniques used for dyeing of PP are:

- (i) Spin coloration
- (ii) Physical modification
- (iii) Chemical modification
- (iv) Dyeing of unmodified fibres.

Table 2.5 Improvement in dyeability of PP by blending with various polymers during melt spinning

Polymer blended	Improvement
Oligocyclopentadiene	Dyeability with disperse dyes
Nylon 6 and 6,6	Dyeability with acid dyes
Poly(ethylene-covinyl acetate) (EVA)	Dyeability with disperse dyes, dye uptake, light- fastness, wash-fastness, etc. depending on the proportion of EVA in melt blend.
Poly butylene thereptalate (PBT)	Dyeability with disperse dyes
Cationic-dyeable polyester(CDP)	Dyeability with cationic dyes

Physical modification of PP to confer dyeability includes:

- (i) Melt blending
- (ii) Blending with polymers and copolymers
- (iii) Blending with dendritic polymers
- (iv) Incorporation of metals.

2.17.1 Melt blending

Melt blending of PP with small percentages of polyester and polystyrene brings about considerable changes in the crystallinity of PP. The addition of 5% polystyrene reduces the crystallinity as high as 50%. PP may be blended with various dyeable polymers before melt spinning and the corresponding improvements in the dyeing properties of the blended PP are shown in Table 2.5. However, blending brings about a decrease in tensile characteristics which may be controlled by careful selection of blending ratios.

2.17.2 Blending with polymers and copolymers

One practical approach is to physically modify the fibre by introducing a dye fixing additive prior to extrusion. This method requires that the dyed additive particles be microscopically dispersed in the body of fibre so that the whole fibre gives the appearance of being coloured. PP could be modified with styrene-amine resin propimid, which can be dyed well with acid dyes in spite of the hydrophobicity of PP.

2.17.3 Blending with dendritic polymers

An extremely high degree of branching is the typical characteristic of the dendritic polymers. The degree of branching of dendrimers is maximal and

their structure is perfectly regular. For industrial purposes two synthetic routes are economically feasible which are poly (propylene imine) dendrimer and hyper-branched polyester amides.

All dendritic polymers possess typical distinguishing characteristics such as an approximately spherical shape, a high number of reactive end-groups, a high number of branching points and the possibility to take up guest molecules between branches. The dendritic polymers compatible with PP were made by reacting their end-groups with fatty acids. For this purpose amine terminated poly (propylene imine) dendrimers were converted into fatty amides, and OH-terminated hyper-branched poly (ester amides) into fatty esters. The acid dyes combine with fatty amide modified poly (propylene imine) dendrimers. These dendrimers containing a basic tertiary amine group at each branching point form sites for acid dye molecules. The disperse dyes can be taken up by PP modified with poly (propylene imine) dendrimers and hyper-branched poly (ester amides).

2.17.4 Incorporation of metals

Organo metallic compounds containing polyvalent transition metals capable of forming chelates with selected dyes have been widely used. Nickel, aluminium and cobalt, when added to PP, act as excellent reaction sites for chelation which provides improved dyeability

2.18 Dyeing of elastomeric fibres

Spandex, also known as elastane, and often sold under the brand name of Lycra®, is an elastomeric polyurethane. Even in very small proportions, it enables fabrics containing it to stretch. Fabrics that contain spandex can be easily damaged by heat. Typical washing instructions for spandex call for avoiding all temperatures above 40°C. Higher temperatures, up to 140°F (60°C), are used in industrial dyeing of spandex. Polyurethane can be dyed with 1:2 metal-complex monoazo dyes, such as the acid dyes that make up part of the Lanaset range of dyes for wool. When the cotton in a cotton/spandex blend is to be dyed, industrially, without colouring the spandex (spandex reserve dyeing) direct dyes can be used, at a pH around 8.0, along with the additive known as syntan to help prevent staining of the polyurethane. When both the cotton and the spandex in the blend are to be dyed in the same colour, pre-metallised or milling acid dyes are applied at a pH of 4.0, followed by direct dyes at a pH of 8.0.

2.19 Future trends

Application of supercritical fluids to polymer processing has received significant attention since the 1980s. Among them supercritical fluid polymer impregnation has been developed and is now on the verge of practical application. Supercritical fluid dyeing (SFD) was studied in 1990s throughout the world (Saus *et al.*, 1993). The conventional wet-dyeing method must fade out soon because the conventional dyeing of polyester textile requires a lot of dispersing agents and surfactants producing a lot of hard-to-destroy poor biodegradable wastewater. On the other hand, the environmentally friendly supercritical fluid dyeing does not require any water, dispersing agents or surfactants in the dyeing process. It can also save energy as it does not require any drying stage after dyeing.

During a research project supported by the Italian government (Ecotint Consortium) in the field of supercritical dyeing of PET textiles, preliminary experiments were conducted on a laboratory scale followed by a larger pilot-plant scale (Banchero *et al.*, 2008). Experimental results showed that equilibrium partition is more favourable to the fibre than the supercritical bath and increases at high temperatures and low densities range. The choice of the proper working conditions is, anyway, a compromise between a high value of the partition coefficient and an acceptable level of the dye solubility in the dyeing bath, to guarantee a rapid and uniformly dyed product. The drastic reduction in total dyeing time during pilot-plant trial certainly indicates that, on an industrial scale, the productivity of the new process is going to be much higher than that of traditional methods.

However, supercritical fluid dyeing has not as yet been adopted in the world dyeing industry due to the high initial investment cost. Therefore, it may be better initially to apply the SFD to hard-to-dye materials such as aramid, PE and PP fibres and films.

Though extensive studies have been performed by several researchers, only limited basic dye sorption data are available. The amount of dye sorption in polymers in the presence of supercritical carbon dioxide is closely related to both the solubility of dye in the fluids and the distribution of dye between the fluid and the polymer phases. The mobility of dye molecules between polymer chains is generally enhanced due to the swelling of polymers in the supercritical fluids (Chang *et al.*, 1998).

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Abstract: Cellulose is one of the most important textile materials. The colouration of cellulosic textile is a mature and highly efficient industrial technology. This chapter first discusses classification, structure and properties of cellulosic fibres, related to the dyeing of fabric containing this fibre. The chapter then describes main methods of dyeing cellulosic fibres using different dyes and dyeing processes.

Key words: cellulosic fibres, structure, properties, dyeing, dyes.

3.1 Introduction

Cellulose is the most abundant polymer available today worldwide. It is produced by nature at an annual rate of 10^{11} – 10^{12} t, partially in a rather pure form, as for example in the seed hairs of the cotton plant, but mostly combined with lignin and with other polysaccharides, so-called ‘hemi-celluloses’ in the cell wall of woody plants (Klemm *et al.*, 2004).

The colouration of cellulosic textile is a mature and highly efficient industrial technology. A number of distinct cellulosic fibres dyeing processes and classes of cellulose dye have been developed and are particularly cited to certain product types (King, 2007). This chapter discusses these different dyes and dyeing methods for cellulosic fibres.

3.2 Cellulosic fibres

3.2.1 Classification

Cotton

Cotton fibres are the purest form of cellulose, nature’s most abundant polymer. Nearly 90% of the cotton fibres are cellulose. The non-cellulosics are located on the outer layers or inside the lumens of the fibres whereas the secondary cell wall is purely cellulose. The cellulose in cotton fibres is also of the highest molecular weight among all plant fibres and highest structural order, i.e. highly crystalline, oriented and fibrillar (Hsieh, 2007).

Cotton is the fine seed hair of plants of the Mallow family; the fibre serves probably to accumulate moisture for germination of the seed (Cook, 2001). Many species are grown commercially, but they may be conveniently divided into three types by staple lengths: (Type 1) 25–60 mm, (Type 2) 13–33 mm and (Type 3) 9–25 mm (Thomas, 1995).

The fully hydrated fibres are cylindrical and the matured fibres dry into flat twisted ribbon forms. Drying of the fibres involves the removal of fluids from the lumens and intermolecular water in the cellulose. The fluid loss from the lumens causes the cylindrical fibres to collapse to form twists or convolutions (Hsieh, 2007).

Cotton possesses its highest fibre quality and best potential for spinning when the bolls are mature and freshly opened. The quality of baled cotton depends on many factors including variety, weather condition, degree of weathering, cultural, harvesting and storage practices, moisture and trash content and ginning processes.

Bast fibres

The bast fibres form bundles or strands that act as hawsers in the fibrous layer lying beneath the bark of dicotyledenous plants (Cook, 2001). They form a strength-giving protective layer around the woody central portion of the stem, and are themselves protected by an outermost cuticle which contains waxes and other substances. The fibres consist of bundles of thick-walled cells held together by gummy substances. The ultimate fibres vary in dimensions from one species to another (Thomas, 1995).

The strands of bast fibres are normally released from the cellular and woody tissue of the stem by a process of natural decomposition called retting (controlled rotting). Often the strands are used commercially without separating the individual fibres one from another (Cook, 2001).

The crude bast fibres contain less cellulose than cotton (Jute 71.3%, Raw flax 80.1% and Decorticated ramie 83.3%). The intercellular material consists of pectins, hemi-celluloses (both complex polysaccharides) and lignin. Jute is frequently used without further purification, but flax and ramie are usually scoured and sometimes bleached. Flax containing 'sprit' may be difficult to dye level because the flax fibre and sprit differ in dyeability. Jute for dyeing is pre-scoured, but considerable quantities of lignin usually remain, leading to poor light-fastness (Thomas, 1995).

Regenerated fibres: viscose, modal fibres and Tencel

The most abundant source of cellulose is wood, of which it constitutes about 40–50%. For wood fibres to be converted into textile yarns they must first be dissolved in a suitable solvent from which they can be regenerated as

continuous filaments after the solution has been extruded through a fine orifice (Thomas, 1995).

Rayon fibre is defined by the US Federal Trade Commission as 'a manufactured fibre composed of regenerated cellulose, as well as manufactured fibres composed of regenerated cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxyl groups' (US Federal Trade Commission, 2003). Substituents consist of manufacturing impurities, pigments, fire retardants or other additives. Rayon was the first man-made fibre. In 1924, rayon was adopted officially by the National Retail Dry Goods Association; before that time, it had been termed artificial silk, fibre silk, wood silk or viscose silk. Rayon fibres are a diverse group, all consisting of regenerated cellulose derived from wood pulp. The basic fibre properties of rayons vary, particularly with respect to wet and dry tenacity, elongation, elastic recovery, water and alkali swelling and, to some extent, abrasion resistance. They have certain characteristics in common that are attributable to their cellulose composition: they are hydrophilic, swell in water and alkali, are responsive to essentially the same dyes as cotton and, when heated, decompose without melting (Marash *et al.*, 2001).

Rayon fibres are made from chemical cellulose (dissolved wood pulp), sodium hydroxide, carbon disulfide and sometimes modifiers, which are usually based on ethoxylated natural fatty acid amines. Most rayon is made by the viscose process; however, some specialty rayon is made by the cuprammonium process in Italy, the former USSR and Japan and by the solvent-spun process in the United States, the United Kingdom and Austria. In the manufacture of the various viscose (wet-spun) rayon fibres, the same basic process is used. However, a number of important variables in the viscose process can be manipulated to obtain fibres of substantially different characteristics. In broad terms, the main fibre categories include regular (conventional) rayon, modified high-tenacity rayon, high-wet-modulus rayon and polynosic rayon.

Regular viscose differs from cotton in being non-fibrillar, having no lumen, and having a much lower degree of polymerisation (DP). The skin contains numerous small crystallites, while the core has fewer but larger crystallites. Under the microscope viscose fibres appear striated longitudinally and in cross-section their circumference is irregularly serrated due to contraction of an originally cylindrical shape during the later stages of their formation. Compared with cotton, regular viscose suffers from the disadvantage of much lower breaking strength, particularly when wet. Although the high-tenacity viscose fibres have been produced for at least half a century, they still had the disadvantages of a low wet modulus, and to overcome this modified high wet modulus (so-called because of modifiers in the spin bath) and polynosic fibres were introduced (Thomas, 1995).

Some of the raw materials used in the production of rayon are recoverable. Carbon disulphide is recovered to various extents by larger plants; on average, 30–35% is recovered, the balance being lost through volatilisation or decomposition. Also, some zinc is collected as a precipitate (zinc sulphide) in the spinning process and is reworked by some producers (Hickman, 1993). However, although efforts by the major producers are expected to reduce carbon disulphide and zinc emissions, increasing environmental concern has centred on the conventional preparation of conventional regenerated cellulosic fibres because still more of the remaining zinc and carbon disulphide needs to be recovered in waste-treatment facilities at the plant site to meet established water pollution regulations.

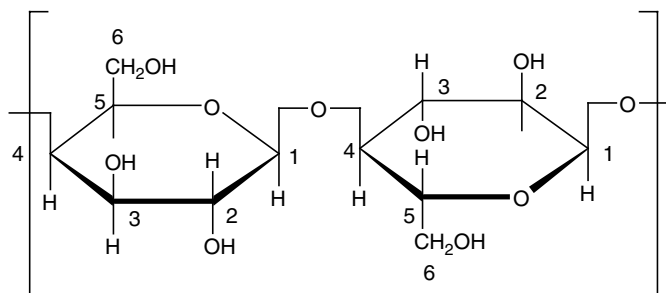
One of the most exciting recent developments in the production of regenerated cellulosic fibres has been the introduction of an alternative to the viscose process considering the objectionable effects of viscose manufacturing plants on the environment (Loubinoux and Chaunis, 1987). Courtaulds PLC has established a successful regenerated cellulosic fibre manufacturing process using N-methyl-morpholine-N-oxide (NMMO) as a solvent for wood pulp (Taylor and Mears, 1991). The solvent is totally recoverable for reuse so that the process is environmentally innocuous. The fibre was named as Tencel by Courtaulds. It is fibrillar in structure and approximates to cotton in its behaviour under stress and capacity for absorbing liquid water even more closely than modal fibres (Thomas, 1995).

3.2.2 Structure and properties

The structure of cellulose, although one of the most unique and simple in the field of polysaccharides, has a rather remarkable and complex influence on the course of chemical reaction of this polymer. Moreover, the structure is responsible for the macroscopic properties of the polymer (Klemm *et al.*, 2004).

The main features of the chemical structure of cellulose are well known. It may be most conveniently described as a 1,4- β -D-glucan, i.e. a condensation polymer of β -D-glucopyranose with 1,4-glycosidic bonds (see Fig. 3.1) (Thomas, 1995). The very long chain that is limited in rotational freedom about the anhydrogluco-pyranose C-O-C link leads to a rigid and highly crystalline structure. The abundant hydroxyl groups, one C-6 primary and two C-2 and C-3 secondary on each anhydroglucose unit, allow extensive intermolecular and intramolecular hydrogen bonding to further enhance the cellulose structure for strength. These hydroxyl groups are also critical chemical characteristics of cellulose fibres as they bond water and are responsible for the chemical reactivity such as in chemical modification, dyeing and finishing (Hsieh, 2007).

The degree of polymerisation of cellulose varies with its source and is usually expressed as an average, since a wide distribution is found in most samples. In native cellulose it may be as high as 14 000, but purification



3.1 Chemical structure of cellulose.

involving treatment with alkali usually reduces this to about 1000–2000. The DP of cellulose regenerated by the older methods is about 250–300, but that of modal fibres is higher (about 500–700). The regenerated cellulose differs from native cellulose only slightly and the differences in properties arise mainly from differences in supramolecular structure (Thomas, 1995).

Knowledge of the fine structure of cellulose is essential for a full understanding of dyeing processes since it is important to know precisely where a dye becomes attached to the fibre. It is generally accepted that reagents cannot penetrate the crystalline regions unless they can simultaneously disrupt them (Holme, 1967; Peters and Ingamells, 1973). The dyeing properties of fibrous polymeric materials depend on the relative amount of the amorphous phase and the chain packing, especially in the intermediate phase between crystalline and amorphous phases. Both structural parameters strongly affect the sorption characteristics of fibrous polymers on solvent and dye molecules. Because the molecular orientation provides information on the degree of chain packing in both the crystalline and intermediate phases, birefringence measurements are conducted to measure the degree of orientation of the fibrous polymers. The higher birefringence value means the higher chain packing efficiency of fibres results in poor dyeability since the regions of cellulosic fibres are more ordered, and therefore less accessible. Also, the higher value of the crystallinity of the fibre indicates lower solvent-processing characteristics and dyeability.

The most obvious macro-structural feature to affect the dyeing of a fibre is its specific surface area, which is inversely related to its fineness. It has been known for over 65 years that the finer the fibre, the greater is the rate of dyeing (Thomas, 1995).

3.3 Main methods of dyeing cellulosic fibres

Cotton and other cellulosic fibres are dyed with more types than for any other fibre. There are water-soluble dyes applied by a one-bath process without the use of mordants (direct dyes), water-soluble dyes that form

a chemical linkage with the fibre (reactive dyes) and water-insoluble pigments that are applied as water-soluble precursors which are converted to the insoluble pigment after diffusion into the fibre (vat dyes, azoic dyes and sulphur dyes) (Ingamells, 1993). Each of these classes of dye has its own application methods, dyeing characteristics, cost, fastness properties and colour range, and therefore its own particular advantages and disadvantages. Within each group, application and performance properties vary considerably so the choice of which dyes to use is often not easy (Broadbent, 2001).

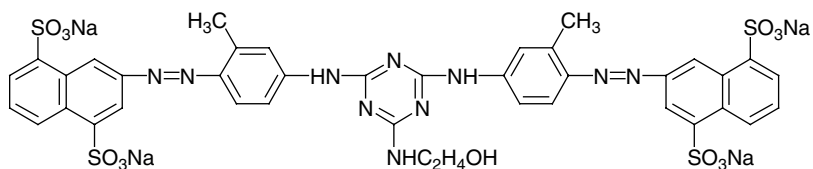
3.3.1 Direct dyeing

Direct dyes are so named because they have natural affinity for cellulose and can be applied without using any auxiliary chemicals. In practice, the dyeing rate and colour yield can be greatly improved by adding inorganic salts such as sodium chloride or sodium sulphate to the dyebath.

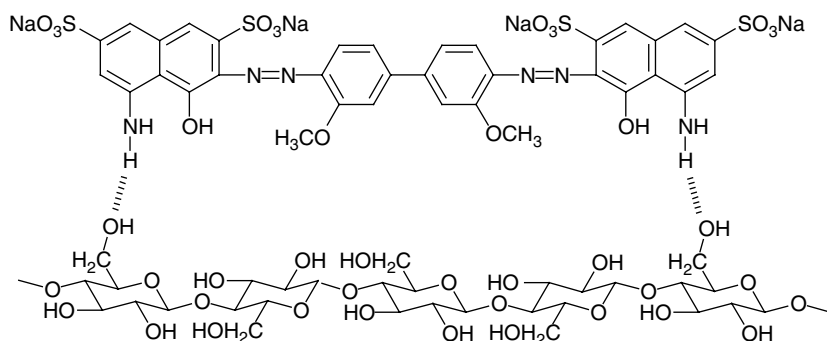
The affinity of a direct dye is determined as a measure of the distribution between fibre and dyebath under standardised dyeing conditions in equilibrium, and represents the difference between the dye affinity to water (hydrophilicity) and to cellulose (Rouette, 2000).

The molecules of direct dyes are similar in structure to those of acid dyes but they are larger (see Fig. 3.2). It is their size that distinguishes them from acid dyes and makes them substantive to cellulose. Their attachment is through both hydrogen bonds and van der Waals forces and the intensity of the latter increases with increasing molecular size (see Fig. 3.3). Their hydrogen bonding capability is also aided by their long flat molecular structure which enables them to lie along a cellulose chain in register with hydroxyl groups (Ingamells, 1993).

The greatest advantage of direct dyes is simplicity of application and low cost. They are available in a full range of hues but are not noted for their colour brilliance. Their major drawback is their poor to moderate fastness to washing. This limits their use to materials where good wash-fastness is not critical. The light-fastness of dyeing with direct dyes on cellulosic fibres varies from poor to fairly good, although some copper complex direct dyes have very good light-fastness.



3.2 An example of direct dye (C.I. Direct Yellow 86).



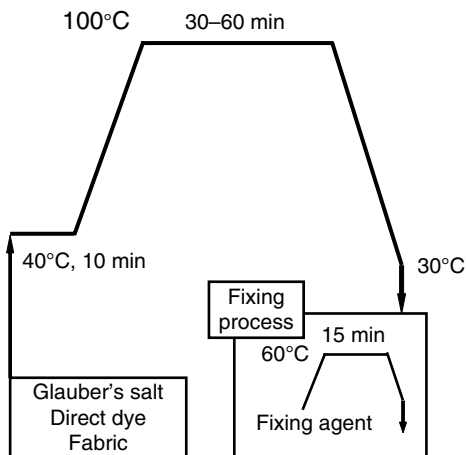
3.3 Principle of direct dyeing of cellulose.

Wash-fastness of direct dyes is improved by resin treatment of dyed fabrics or by various after-treatments. In some cases, however, such after-treatments decrease the light-fastness. They also invariably cause a change in hue that makes shade correction and colour matching more difficult.

This class of water-soluble anionic dyes has fairly high affinity for cellulosic fibres, particularly under favourable dyeing conditions (10–20 g/L electrolyte); thus part of the dye originally dissolved in the dyebath has exhausted onto the fibre at equilibrium. In the complete absence of electrolyte, some direct dyes will not dye cellulose properly since the negatively charged cellulosic fibres repel the similarly charged ion of the substantive dye in water. This is why the application of direct dyes always involves common salt (sodium chloride) or Glauber's salt (sodium sulphate) as a component of the dyebath. Electrolytes reduce the charge on the fibre, thus facilitating the approach of the dye ion to within the range at which H-bonding or van der Waals forces can become effective. The more sulphonic acid groups there are in the dye molecule, the greater will be the effect of electrolyte and the greater the care needed to obtain level dyeings.

Dyeing with direct dyes is carried out in neutral solution. The dyebath is gradually heated to promote diffusion and levelling of the dyes, usually with gradual salt addition to exhaust the dyebath. Figure 3.4 shows a typical direct dyeing profile.

However, the dye–fibre bond is very unstable and the wet-fastness properties are poor. The lack of wet-fastness of direct dyes is undesirable for many purposes, particularly for materials which will be expected to withstand washing. After-treatment of dyeing of direct dyes on cellulosic materials aims to improve the wash-fastness by increasing the dye's molecular weight. This makes it less soluble and of slower diffusion. Some of these processes decrease the light-fastness of the dyeing. After-treatments are difficult and costly to carry out, and often give changes in hue that greatly impede shade correction and colour matching. Many of the direct dye



3.4 Direct dyeing profile.

after-treatments now have limited use because reactive dyes result in dyeing with much better wash-fastness (Broadbent, 2001). After-treatment methods include diazotisation and development, coupling with diazonium salts, after-treatment with formaldehyde, metal complex formation, cationic fixatives, and resin and cross-linking agent.

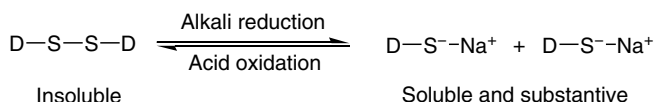
3.3.2 Sulphur dyeing

Sulphur dyes are complex organic compounds synthesised by heating simple amines or phenolic compounds in the presence of sulphur. The structure of the chromophore of sulphur dyes is complex and unknown.

Sulphur dyes exist as a pigment form and they are converted to the sodium salts of the leuco-dyes having affinity for cellulose by treatment with a reducing agent under alkaline conditions (see Fig. 3.5). After the leuco-dye anions have been adsorbed onto the cellulose and have diffused into it, they must be oxidised back to their insoluble pigment form. The chief advantages of sulphur dyes are their cheapness and their general good fastness to washing. The biggest limitation of sulphur dyes is that they are not bright enough in colour for many uses. Especially in the case of black sulphur dyes, the dyed material stored under conditions of high humidity and temperature can lose its natural strength probably due to inadequate washing off after dyeing (Ingamells, 1993).

The application of sulphur dyes consists essentially of the following steps (Christie *et al.*, 2000):

- (a) Reduction to the soluble leuco form.
- (b) Impregnation of the fibres with the leuco compound.
- (c) Oxidation in the fibres to the insoluble form.



3.5 Principle of sulphur dyeing.

Some sulphur dyes are marketed already in the leuco form and are soluble in water. With these dyes, step (a) has already been carried out by the dye manufacturer.

The dyebath can be made by diluting the leuco form product to the concentration required for dyeing. The reduced form of sulphur dye is applied to the cellulosic fibre in the presence of sodium chloride and a penetrating agent. Often the liquor is brought to the boil in the early stages of dyeing, maintained at the boil for about 30 min and then gradually allowed to cool (Christie *et al.*, 2000). Once the leuco form has been adsorbed, the fabric is exposed to the atmosphere, where oxidation generates the mechanically entrapped insoluble pigment (Ingamells, 1993). Exposure to air usually suffices, but in a few cases specific oxidising agents have to be used. The desired reaction in oxidation of sulphur dyes is conversion of the thiol groups to disulphide groups.

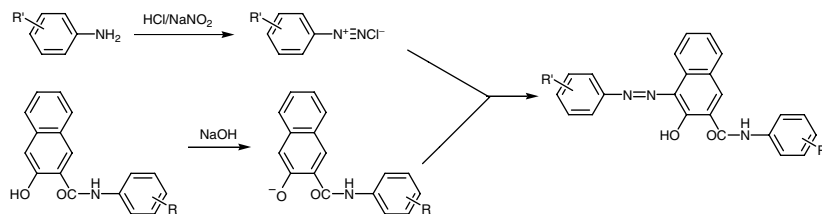
The sulphur dyeing process is very important for cheap staple goods or heavy fabrics of cotton in muted shades which are fast to washing, light and abrasion, but less so for regenerated cellulose fibres due to the losses in handle and lustre (Rouette, 2000).

3.3.3 Azoic dyeing

Azoic dyes are pigments that are synthesised inside the fibre by two components neither of which is a dye itself. The two components are an aromatic diazonium salt and an aromatic hydroxyl compound, often a naphthol. Although the coloured material produced in azoic dyeing is a pigment, the azoics are classified as dyes because the naphthol component has affinity for cellulose and is applied like a dye before the diazo component is added.

Unlike vat and sulphur dyes, whose whole chromophore is temporarily water-soluble, and is applied on the fibre in the soluble state, azoic dyes are formed directly on the fibre by the reaction (coupling) of two usually colourless components of limited water solubility (see Fig. 3.6). The azo compound formed inside the fibre by this reaction is a pigment which is fast to washing mainly because it is extremely insoluble in water (Perkins, 1997).

The greatest advantage of azoic dyeing is that it provides an economical way to obtain certain shades, especially of red. The main disadvantages of



3.6 Principle of azoic dyeing.

this dyeing method are the limitations of hue selection, complicated and time-consuming application procedures, and poor fastness to crocking.

The batch dyeing of cellulosic fibres using an azoic combination involves four steps (Broadbent, 2001):

- 1 Absorption of the naphtholate ion by the cellulose.
- 2 Removal of the excess naphthol solution from the fibre surfaces.
- 3 Treatment with the diazonium ion solution to bring about coupling.
- 4 Soaping the fabric at the boil to remove superficial pigment, followed by rinsing and drying.

However, the most important method for dyeing azoic combinations is continuous treatment of fabrics. For example, fabric can be padded with coupling component, dried and padded with diazo component followed by washing off. The azoic dyeing methods have declined significantly in popularity probably due to substitution with reactive dyes.

3.3.4 Vat dyeing

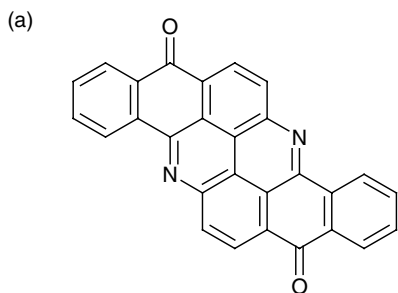
Vat dyes and sulphur dyes are similar in that they are both pigments which must be reduced and oxidised during application. The vast majority of vat dyes are based on the anthraquinonoid or the indigo chromophores (see Fig. 3.7).

Despite their complex molecular structures, vat dyes have one common feature: they all contain the carbonyl group. Vat dyes can therefore be reduced to leuco forms, whose molecules possess hydroxyl groups. Although the leuco form is insoluble in water, it can be rendered soluble in alkali and the dissolved material can be oxidised back to the original vat dye (see Fig. 3.8).

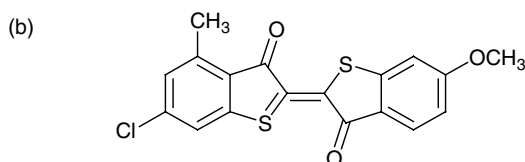
Vat dyes have outstanding wash-fastness and light-fastness as a class. An exception is the vat dye indigo which has very poor wash-fastness. The biggest disadvantage of vat dyes is their relatively high cost.

Application of vat dyes requires the following steps (Christie *et al.*, 2000):

- (a) Preparation of the sodium derivative of the reduced (leuco) compound (vatting).

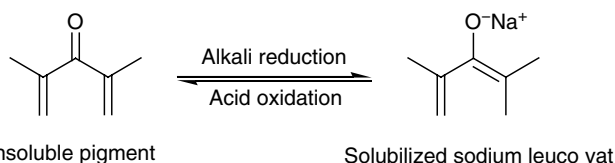


Anthraquinonoid dye (C.I. Vat Yellow 1)



Indigoid dye (C.I. Vat Red 6)

3.7 Examples of vat dyes: (a) Anthraquinonoid dye (C.I. Vat Yellow 1).
(b) Indigoid dye (C.I. Vat Red 6).



3.8 Principle of vat dyeing.

- (b) Impregnation of the fibres with the leuco compound.
- (c) Oxidation in the fibres to the insoluble vat dye.
- (d) Rinsing and soaping.

With solubilised vat dyes, step (a) is omitted.

The order in which these steps are performed depends on the dyeing method employed. The two general dyeing methods are called the pigment method and the reduced method. In the pigment method, the vat dye dispersion in pigment form is distributed in the material to be dyed. After the pigment is uniformly distributed in the material, the dye is reduced so that the dye can be absorbed by the fibres. In the reduced method, the dye is reduced to the soluble, leuco form before coming in contact with the material to be dyed. The material is then contacted with the reduced dye, and the dyed is absorbed by the fibres. The dyeing process may be either batch or continuous (Perkins, 1997).

3.3.5 Reactive dyeing

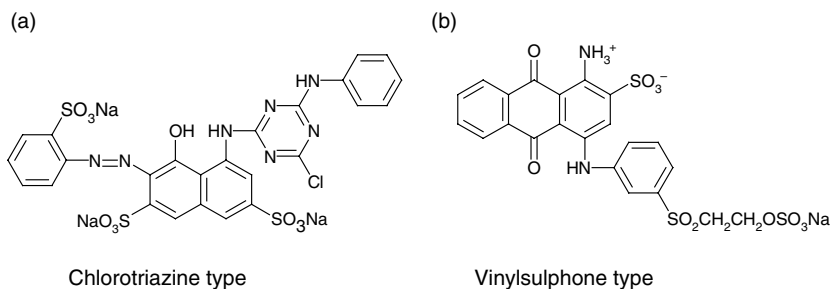
Reactive dyes are relatively new, having been developed in the 1950s. They are sometimes called 'fibre reactive dyes'. As the name implies the reactive dyes chemically react with the fibre forming covalent bonds. These dyes combined ease of application, previously unobtainable shades and very high levels of fastness.

Reactive dyeing differs from all other applications of water-soluble dyes insofar as the final goal is to achieve a dye–fibre covalent bond. Much smaller molecules than direct dyes are suitable for use as reactive dyes because one covalent bond is about 30 times as strong as one van der Waals bond. The energy required to break these bonds is of the order of 70–200 kJ mol⁻¹, which explains their excellent wash-fastness (Lewis, 1998). Also, reactive dye molecules confer very bright colours to dyeing because the molecules need be no larger than those of simple acid dyes.

During the early years of development of reactive dyes it was soon recognised that the important reactive systems could be classified into two distinct categories, depending on the mechanism of formation of the dye–fibre bond and the stability of this bond to subsequent treatments. Reactive groups are of two main types (Broadbent, 2001):

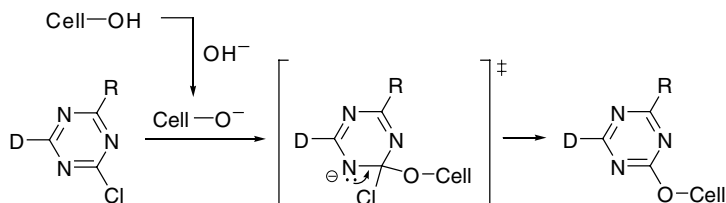
- 1 Those reacting with cellulose by nucleophilic substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a heterocyclic ring.
- 2 Those reacting with cellulose by nucleophilic addition to a carbon-carbon double bond, usually activated by an adjacent electron-attracting sulphone group.

The reactive structures, some important examples of which are shown in Fig. 3.9, are attached to the rest of the dye molecule by bridging groups such as imino –NH–, substituted imino and amide linkages, –NH–CO–.



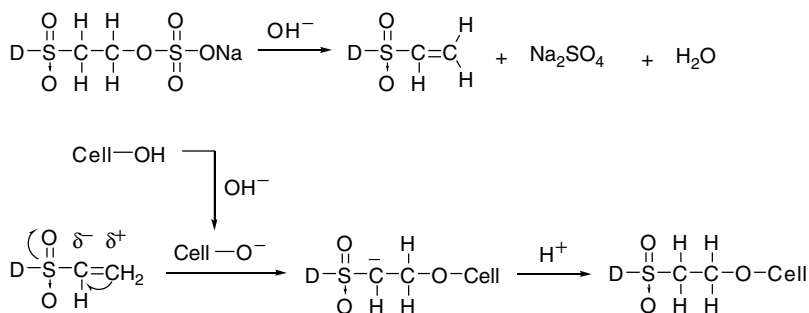
3.9 Examples of reactive dyes: (a) Chlorotriazine type. (b) Vinylsulphone type.

(a)



S_N2 substitution of monochlorotriazine type reactive dyes

(b)



Nucleophilic addition of vinylsulphone type reactive dyes

3.10 Principle of reactive dyeing of cellulose (D = dye chromophore):

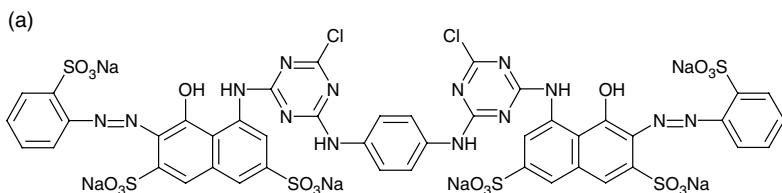
(a) S_N2 substitution of monochlorotriazine type reactive dyes. (b)

Nucleophilic addition of vinylsulphone type reactive dyes.

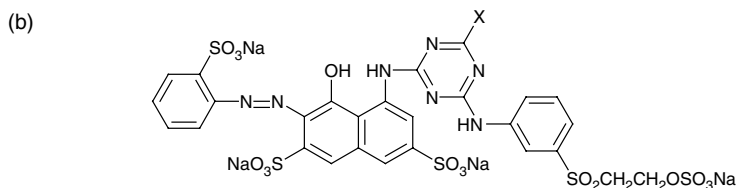
Two reaction mechanisms give rise to a covalent bond between cellulose and dye which in terms of degree of fixation, rate of fixation and stability of the dye-fibre bond complies with industrial requirements: nucleophilic S_N2 substitution and nucleophilic addition (see Fig. 3.10). In nucleophilic S_N2 substitution, a mobile halogen atom of the dye is substituted by the ionised nucleophilic oxygen group of the cellulose (Cell-O^-).

In nucleophilic addition, a proton and the ionised oxygen group of the cellulose are added to the active group of the dye. The best-known dyes of this group – the vinyl sulphones – carry a protective group, which is eliminated even at a fairly low pH and sets the reactive group free during dyeing.

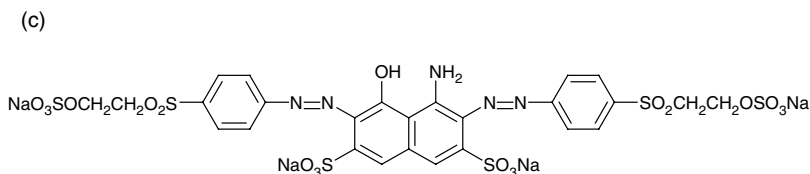
The degree of fixation of monofunctional dyes on the fibre is around 70% while that for bifunctional dyes can be as high as 98%. Within the range of products offered by dye producers, bifunctional or even polyfunctional alternatives are appearing more and more in addition to the monofunctional reactive dyes. Bifunctional reactive dyes are classified into two groups: the homobifunctional and the heterobifunctional dyes. Both aromatic



C.I. Reactive Red 120 (MCT/MCT)



C.I. Reactive Red 194 (MCT/VS)



C.I. Reactive Black 5 (VS/VS)

3.11 Examples of bifunctional reactive dyes: (a) C.I. Reactive Red 120 (MCT/MCT). (b) C.I. Reactive Red 194 (MCT/VS). (c) C.I. Reactive Black 5 (VS/VS).

heterocycles and vinylsulphones (VS) are used as reactive groups (see Fig. 3.11). The following combinations are known (Rouette, 2000):

MCT/MCT (Monochlorotriazine/monochlorotriazine)

MCT/VS (Monochlorotriazine/vinylsulphone)

VS/VS (Vinylsulphone/vinylsulphone)

FT/VS (Fluorotriazine/vinylsulphone)

FCP/VS (Fluorochloropyrimidine/vinylsulphone).

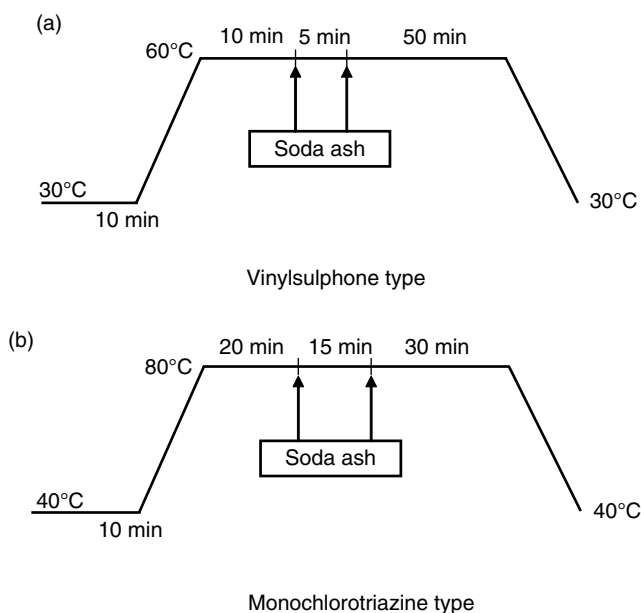
Bifunctional reactive dyes are a useful development from an ecological point of view, because the high degree of fixation means that the proportion of dyes lost via effluent can be minimised. This also means that the costly treatment of effluent contaminated with dye can be drastically reduced (Rouette, 2000).

Several dyeing processes are used for reactive dyeings such as the batch-wise process, pad-batch process and continuous process.

The general principle of batchwise or exhaust dyeing with reactive dyes is to encourage as much dye as possible to move into the fibre over a period of 30–45 min by adding a high concentration of salt to the neutral dyebath. During this period, the dye does not react with the fibre and migration from fibre to fibre is possible. Consequently most of the dye is exhausted onto the fibre before the alkali is added, thus providing the best possible conditions for fixation before the dye–fibre reaction is initiated. Once the levelling process is complete, alkali is added and fixation continues for a further 30–60 min (see Fig. 3.12) (Ingamells, 1993). The covalent bond between cellulose and dye that results from this is much more resistant to the usual conditions of use than the physicochemical bond between direct dyes and cellulose.

The pad-batch process is essentially a semi-continuous one. This important process represents the minimum possible investment for dyeing large yardages of cellulosic fabrics with cold dyeing, highly reactive dyes (Aspland, 1997). Pad-batch dyeing involves padding the fabric with a pre-mixed alkaline solution of the reactive dyes and then winding up the impregnated fabric onto a perforated or unperforated beam, covered with a plastic sheet to prevent drying out. Fixation occurs during storage of the batched fabric at ambient temperature. The colouration process is then completed by washing the dyed fabric free of alkali and loose dye.

A representative reaction of dye and cellulose was shown in Fig. 3.10. The side-reaction with hydroxyl ion is undesirable as the hydrolysed dye will

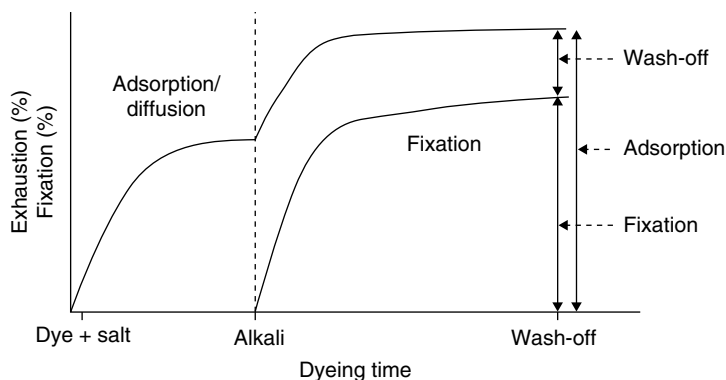


3.12 Reactive dyeing profiles: (a) VS type. (b) MCT type.

have a lower fastness on the fibre, being the equivalent of direct dye. The typical exhaust process for dyeing cellulose with reactive dyes is similar to that for direct dyes. The goods are loaded in the machine with appropriate auxiliary chemicals and the dyes are added after equilibration.

Figure 3.13 shows the exhaustion and fixation behaviours of reactive dyes. The generally accepted model for dyeing of reactive dyes into cellulosic fibres consists of two phases: (a) adsorption and diffusion phase and (b) fixation phase. The former is controlled by varying the dyeing time, the dye-bath temperature and the salt concentration, and the latter is achieved by the selection of an appropriate alkalinity (Ingamells, 1993).

Reactive dyes are usually applied with the addition of electrolyte and the extent to which reactive dyes are affected by the addition of electrolytes to the dyebath is known as salt sensitivity. The addition of electrolyte increases the rate of strike of the dye; when cellulose is immersed in a solution of a reactive dye it absorbs dye from the solution until equilibrium is attained, and at this stage most of the dye is taken up by the fibre. Cellulose carries a negative charge in pure water. As the dye is also anion, hence negatively charged, there is electrostatic anion-anion repulsion between dye and cellulose. Therefore, by adding inert electrolyte such as common salt or Glauber's salt to the dyebath, this electrostatic barrier, known as the Donnan potential, can be largely suppressed, facilitating dye-fibre contact and allowing better interaction of the Yoshida and van der Waals forces and hence improving substantivity. The diffusion coefficient of the dye is therefore a function of both dye and electrolyte concentration (Johnson, 1989). The dye exhaustion (%) value of reactive dye is a linear function of salt concentration particularly at lower dye concentrations within the cellulose in the presence of a fixed amount of added dyes, although the slope decreases with increasing salt concentration. It is considered that the initial rapid rise is due to the response of dye to the lowering of electrical potential barrier to diffusion as the concentration of electrolyte



3.13 Exhaustion and fixation behaviours of reactive dyes.

increases. In the adsorption and diffusion phase, the reactive dye is adsorbed onto the cellulose surface and then diffuses into the fibre matrix. This phase is completely reversible, i.e. dye molecules are in equilibrium between fibre and dyebath. Any change in bath composition (e.g. amount of electrolyte, pH, temperature, etc.) has an instantaneous effect on the behaviour of the dye.

If conditions are favourable (high temperature and/or high pH), the reactive dye reacts with active sites in the cellulose (hydroxyl groups) in fixation phase, resulting in a strong covalent bond. At the same time as the principal reaction between dye and fibre, subsidiary reaction take place, usually affecting fastness properties.

To obtain the required fastness properties, inactivated adsorbed dye molecules must be washed off the fibre in the washing-off phase. They would otherwise lead to poor wet-fastness properties because their molecules are bound to the fibre by weak physicochemical forces. In this phase, care must be taken to ensure that the pH is neutral by completely washing off the fixation alkali and thus preventing gradual alkaline hydrolysis of the dye–fibre bond or even fibre damage.

3.4 Future trends

Concern for a sustainable future is real and not a passing fashion trend. This is a complex issue but momentum is growing, and is driven by issues such as the depletion of natural resources, climate change and energy security. Like any other industry in the global economy, textiles and apparel will have to adopt sustainable and responsible business practices. In the long run they will be challenged and must respond and be seen to be serious about the planet's future (Taylor and Kininmonth, 2009).

The conservation of energy is one essential step we can all take towards overcoming the mounting problems of the worldwide energy crisis and environmental degradation. To improve margins and gain competitive advantage, it is necessary to adopt a new approach. Modification of existing processes/equipment or the purchase and installation of new equipment may be considered, to reduce the consumption of energy, water and process chemicals. The combination of efficient energy-conservative measures, Right-First-Time production technologies and highly productive processes has the potential to drive down the total cost of production (Maurya, 2010).

Cleaner colouration with minimal effluent load is one of the principal issues for sustainability. The main effluent-control parameters of textile dye-house wastewater include volume, total dissolved solids, chemical oxygen demand (COD), biological oxygen demand (BOD), colour and pH. Each is quantifiable and normally limits are established, which may not be

exceeded in effluent discharge to either municipal wastewater treatment plants (WWTP) or to surface waters (Taylor and Kininmonth, 2009).

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Dyeing of textile fibre blends

N. A. IBRAHIM, National Research Centre, Egypt

Abstract: The fourth chapter deals with dyeing of blends. Factors affecting blends dyeing such as fibre blend components and their proportions, pre-treatment, key issues of dyeing blends, major dye combinations, main methods of dyeing and major type of coloured effects are discussed in detail. Recent developments and possible future trends are covered in brief. In addition, sources of further information are provided.

Key words: fibre blends, blends dyeing, dyeing processes and equipments, future prospects.

4.1 Introduction

Blending of textile fibres is carried out to attain aesthetic colour effects, to minimise the total production cost, as well as to improve the performance properties of the obtained textile products. Factors affecting the choice of proper dyestuffs as well as dyeing conditions for obtaining high-quality blend dyeings include: behaviour of blend components and their proportions towards different dyes and dyeing conditions, compatibility of dyebath ingredients, availability of proper dyeing equipment, the increased demand for novel effects achieved by blending, subsequent finishing treatments, as well as economic realities and ecological concerns.

This chapter addresses the dyeing of blends, and comprises four parts: key fibre blends, key issues of dyeing blends, main methods of dyeing specific blends as well as recent developments and future prospects of blends and their dyeability. Additionally, sources for further information are given.

Classification of textile fibres, fibre blends, advantages of blending and the most common textile blends and their potential uses are highlighted in the first part. The second part gives an overview of pollution prevention measures in pre-treatments, classification of dyestuffs, dyeing auxiliaries, dyeing stages, dye–fibre bonds, colouristic effects, as well as major dye combinations. The third part is concerned with dyeing process stages, dye selection as well as proper dyeing methods for some of the most important fibre blends. The fourth part considers recent developments and future trends for dyeing blends, i.e. development of fibres and fibre blends, and options for

enhancing blends dyeing. Finally, sourcing for further information is given at the end of the chapter.

4.2 Key fibre blends

4.2.1 Textile fibres

Textile fibres are broadly classified into natural and man-made fibres. The most important natural fibres are: cellulosic fibres, e.g. cotton, flax, jute, sisal, etc., protein fibres, e.g. wool, silk, etc., and mineral fibre, e.g. asbestos. On the other hand, man-made fibres can be subdivided into: regenerated fibres, i.e. unmodified (rayon, lyocell) and modified (cellulose acetate and triacetate), synthetic fibres, e.g. polyester, polyamide, polyacrylic, polyurethane, etc., as well as refractory and industrial fibres, e.g. ceramic, carbon, glass, etc. Figure 4.1 shows the chemical structure of the most important textile fibres (Bide, 2009; Paulo and Gubtiz, 2003).

4.2.2 Fibre blending

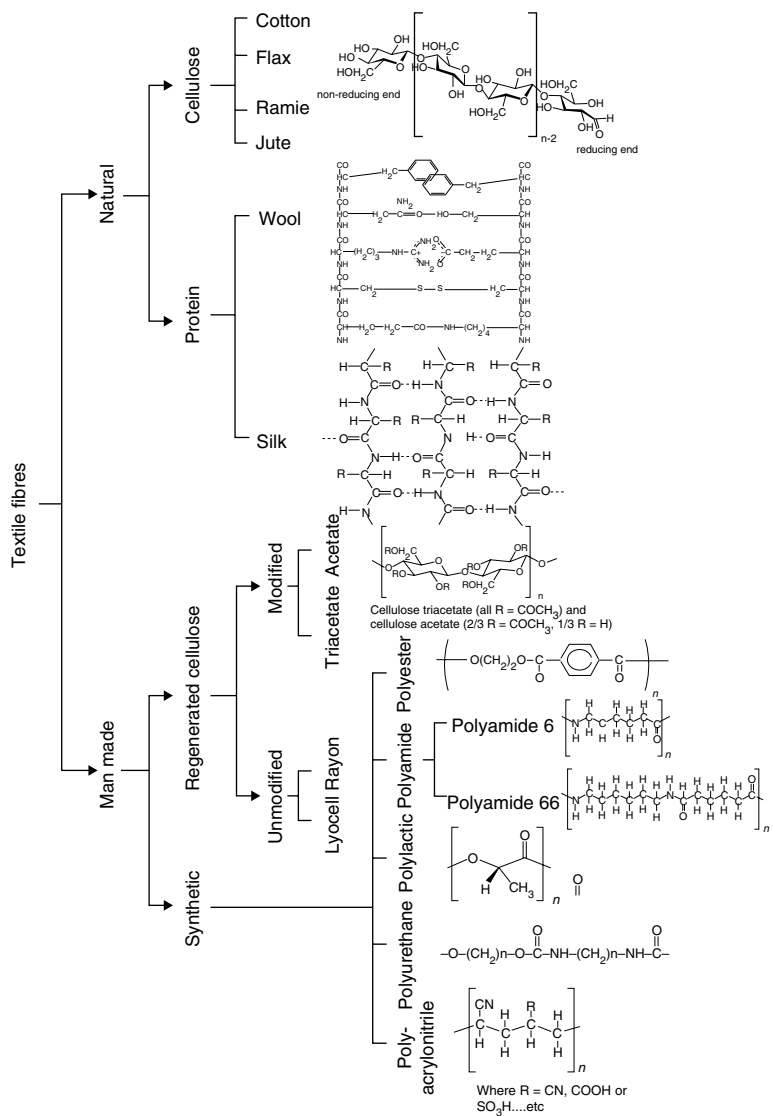
The major goal of fibre blending is to produce a homogeneous single yarn composed of an intimate mixture of two or more similar or dissimilar fibre types for overcoming the drawbacks of the used fibre components along with providing a rich diversity to our day-to-day lives which is partially unachievable using the individual components.

The extent of improvement in blended yarn properties is governed by type of fibre, blending ratio, and mode of blending, i.e. as different filaments or staple fibres in the same yarn, as different yarns, warp and weft, assembled in the same fabric or as core spun yarns (Broadbent, 2001; El-Mogahzy, 2004; El-Mogahzy *et al.*, 2005; Shore, 1998).

4.2.3 Advantages of blending

The increasing demand for fibre blending can be discussed in terms of its positive impacts on:

- Achieving economic advantages via blending of expensive fibres with cheaper ones.
- Enhancing the performance and quality properties via combination of desirable properties of both fibre components.
- Developing novel textile products to meet the demand.
- Prolonging the durability of textile product via incorporation of a more durable fibre component (Choudhury, 2006).



4.1 Textile fibres.

4.2.4 Most common textile blends and potential uses

It would be impossible to provide detailed information about all the various types and possible combinations of textile blends in one chapter. The brief examples of the most important textile blends as well as their potential uses highlighted in Table 4.1 are therefore necessarily selective. On the other hand, proper selection of fibre blend components, blending ratio as well as blending technique ensures production of binary or ternary textile blends with enhanced characteristics and expanded utilisations, e.g. for sport, leisure activities, fashion, apparel, protective clothing, household textiles, etc. (Aspland, 1997; Choudhury, 2006; Shore, 1998).

Table 4.1 Major textile blends and their suitable uses

Blend	Current uses
A. Binary blends	
<i>Man-made/natural (cellulose)</i>	
Polyester/cotton (67/33-woven)	Shirting, outer wear, work wear
Polyester/linen (woven)	Fashion goods, tableware, bed linen
Polyester/cotton (knit)	Sports wear, T-shirts, dress wear
Acrylic/cotton (80/20, 50/50-woven)	Lightweight suits, sports and dress wear
Modacrylic/cotton or viscose (80/20, 50/50-knit)	Underwear, hosiery, leisure clothing
Cellulose acetate/cellulosic	Suits, skirts, dress wear
Viscose/cotton:	
(30/70)	Poplin shirts, blouses, dress and knitwear
(35/65, 50/50)	Terry towelling
Nylon/cotton (10–50/90–50-staple blends)	Dress wear leisure shirts
Nylon filament bas and cotton pile	Weft-knitted towelling
<i>Man-made/natural (protein)</i>	
Polyester/wool:	
(80/20, 55/45-woven)	Suit fabrics
(40/60)	Luxury automotive fabrics
Nylon/wool (20/80)	Woven carpets
Acrylic/fine wool (50/50, 80/20-woven)	Garments
Acrylic/coarser wool	Blanket, floor covering
Viscose/wool	Lightweight suits, dress wear and knitwear
Lyocell/wool	Light summer, sports and leisure wear
<i>Man-made/man-made</i>	
Polyester/viscose (50/50)	Dress goods
Polyester/polynosic	Tubular-knitted fabrics, garments
Polyester/vincel	Rainwear
Acrylic/viscose	Non-crush carpets
Polyester/acrylic (85/15 to 70/30)	Woven or knitted upholstery, sports wear, easy care suits, outerwear, furnishing
Cellulose acetate/viscose	Tropical suits, leisure shirt, underwear

Table 4.1 Continued

Blend	Current uses
<i>Natural/natural</i>	
Cotton/wool: (80/20) (warp/weft)	Washable apparel Blazer cloths, rainwear, shirts, pyjamas
Jute/cotton	Textile furnishing and apparel industries
Wool/ramie (70/30)	Dress fabrics
Wool/silk	High-quality apparel
Silk/cellulose	Upholstery, furnishing, shirting fabrics, women's outerwear
B. Ternary blends	
Nylon/polyurethane (10–20%)/cotton	Knitted underwear
Nylon/wool/viscose	Carpets
Triacetate/nylon/viscose (60/20/20 or 55/15/30-woven)	Shirting, pleated dress wear
Polyester/wool/acrylic (blended staple yarns)	Overcoats, suits
Polyester/cotton warp(65/35)/ acrylic/cotton weft (80/20)	Household textiles
Cellulose acetate/polyester/nylon (25/50/25)	Dress wear fabrics
Cellulose triacetate/polyester/ viscose (65/15/20 or 30/40/30)	Dress wear fabrics

4.3 Dyeing of textile blends

4.3.1 Pre-treatment processes

The major stages for manufacturing textile goods include yarn formation by spinning, fabric formation by weaving or knitting, wet processing, i.e. pre-treatments, dyeing and/or printing, functional finishing and textile fabrication by cutting and sewing. For attaining high-quality dyeings, it is essential that all such impurities, i.e. natural, inherent, added for better spin ability and/or weave ability, as well as other accidental impurities, are removed uniformly along with destroying any trace of colouring matters thereby avoiding any problems and increasing responsiveness of pre-treated substrates to subsequent wet processing such as dyeing, printing and/or chemical finishing. The pre-treatment processes therefore vary for textile blends. The most important operation in pre-treatments is the scouring or cleaning process. Sequence, formulations and conditions of pre-treatments are governed by the fibre type, fabric construction, sizing materials, available equipments as well as the end use of the pre-treated substrates. In case of pre-treatment for attaining dyeings with darker shades, the degree of whiteness is not as important as the cleanliness of the pre-treated substrates.

A high-quality process water as well as the proper choice of textile auxiliaries are essential for efficient removal of different impurities and other contaminants in textile materials, thereby avoiding the most commonly observed dyeing problems such as inconsistent shade, blotchy dyeing, unlevel dyeing, filtering in package dyeing, poor washing off, poor fastness properties, etc. Undoubtedly, high-level pre-treatment is an important requirement for level dyeing, irrespective of the substrate.

Unlike natural and regenerated textile fabrics, synthetic fibre containing fabrics require a special preparatory process, i.e. heat setting, to provide a high degree of dimensional stability along with avoiding creases and folds formed during the subsequent wet processing. Heat setting before scouring could minimise the efficiency of removal of stains, lubricants and sizing agents during the scouring process. An excessive heat setting could cause discolouration, stiffness and/or loss of elasticity, while an insufficient heat setting will give poor fabric stability.

As far as environmental issues are concerned, pollution prevention opportunities dealing with pre-treatments are focused on:

- Good housekeeping.
- Quality control of incoming raw materials, e.g. fibres, yarns, fabrics.
- Pre-screening chemicals before use.
- Process rationalisation, optimisation and/or modification.
- Replacement of hazardous chemicals with eco-friendly ones, e.g. NaOCl by hydrogen peroxide or peracetic acid, non-biodegradable substances by biodegradable ones, harsh chemicals by specific enzymes (α -amylase, pectinase, cellulases, lipases, proteases).
- On-site recovery, e.g. size, soda, wool-wax, heat recovery.
- On-site reuse, e.g. clean washing water after H_2O_2 – bleaching, dyebath reuse.
- On-site recycling of reworkable or non-reworkable as well as hard wastes.
- Machinery selection, e.g. countercurrent washing, low material-to-liquor ratio systems and continuous ranges.
- Employee training with emphasis on pollution prevention practices (Choudhury, 2006; Ibrahim *et al.*, 2004a, b, 2008a; Krizmann *et al.*, 2005; Scarborough and Mathews, 2000; Shamey and Hussein, 2005; Vigo, 1994).

4.3.2 Dye classification

Textile dyes may be classified according to their:

- (i) chemical structure, e.g. azo dyes, anthraquinone dyes, xanthene dyes, indigo and thioindigo dyes
- (ii) method of application, e.g. reactive, direct, acid, basic, vat and disperse dyes.

4.3.3 Dyeing auxiliaries

To attain high-quality dyeings, proper dyeing auxiliaries should be precisely used. The potential functions of dyeing auxiliary products – e.g. surfactant, electrolytes, oxidants, reductants, buffers, deformers, sequestering and solubilising agents, levelling agents, retarding agents and anti-precipitant – include the following (Baldwinson, 1990):

- (i) Improving the efficiency of the pre-treatment processes for subsequent dyeing.
- (ii) Enhancing the extent of dye uptake and fixation.
- (iii) Ensuring the stability of the dyeing bath as well as compatibility of its ingredients.
- (iv) Modifying the textile substrate and/or avoiding its damage.
- (v) Upgrading the fastness properties of the obtained dyeings.
- (vi) Minimising the environmental impacts of textile wet processing, especially dyeing.

4.3.4 Dyeing stages

The dyeing process of textile substrates comprises four stages (Choudhury, 2006):

1. Transport of the dye molecules from solution to the substrate surface.
2. Dye adsorption on the substrate surface.
3. Diffusion or penetration of the dye from the substrate surface to the interior of the fibre through its amorphous regions.
4. Fixation of the dye onto and/or within the substrate via covalent bonds, hydrogen bonds, ion-exchange or van der Waals forces, or through insolubilisation of the pre-dissolved dye inside the fibre.

4.3.5 Dye–fibre bonds

The extent of the dye fixation as well as the fastness properties of the obtained dyeings are determined by the mode of interaction between the dye molecules and the textile fibres by one or more of the following mechanisms (Choudhury, 2006):

- (i) Ionic bonding, e.g. acid and basic dyes/protein fibres.
- (ii) Covalent bonding, e.g. reactive dyes/cellulosic fibres.
- (iii) Hydrogen bonding, e.g. direct dyes/cellulosic fibres.
- (iv) Insolubilisation of pre-dissolved dye following their entry into fibres, e.g. vat and sulphur dyes/cellulosic fibres.
- (v) Adsorption of the dye-vapour, e.g. volatile disperse dyes/polyester.

Table 4.2 Major dye classes, dye–fibre affinity and mode of fixation

Application class	Textile fibres	Mode of fixation
Reactive	Cellulosic fibres and wool	Covalent bonds
Direct	Cellulosic fibres	Hydrogen bonds
Acid	Protein fibres, nylon and polyurethane	Ionic bonds
Basic	Acrylic and basic-dyeable polyester	Ionic bonds
Disperse	Polyester, cellulose acetates and other synthetic fibres	Hydrophobic, hydrogen bonds and van der Waals forces
Natural	Cellulosic and protein fibres	Complexation with mordant
Vat (in the reduced form)	Cellulosic fibres	<i>In-situ</i> deposition by oxidation
Sulphur (in the reduced form)	Cellulosic fibres	<i>In-situ</i> deposition by oxidation
Pigment	Cotton, polyester and their blends	By using suitable binder

Application class, textile fibre and dye–fibre bonds are summarised in Table 4.2.

Factors affecting the dyeing process are type of fibre and form of material, dyestuff selection, type and quantity of textile auxiliaries, dyeing conditions, as well as dyeing equipment. The success of the dyeing process depends on achieving correct shade, even distribution of dye molecules throughout the substrate, high fastness properties and no damage to the textile substrate.

4.3.6 Colour effects obtained by dyeing binary blends

Dyeing of textile blends gives rise to four major types of colour effects (Bae *et al.*, 2006; Broadbent, 2001; Shore, 1998):

1. Solid effect, i.e. both fibre components are identically coloured.
2. Reserve effect, i.e. by dyeing one component, and keeping the other fibre as white as possible.
3. Shadow effect, i.e. both components have the same hue and brightness but of varying depth of shades.
4. Contrast effect, i.e. both fibre components are dyed in contrast hues.

4.3.7 Major dye combinations for binary and ternary blends

Table 4.3 demonstrates classification of binary blends that can be dyed with the major dye combinations for obtaining full depth/fast dyeings (Broadbent, 2001; Shore, 1998).

Table 4.3 Recommended dye combinations for proper dyeing of most important binary blends

Binary blends	Dye type combinations
<i>AA blends, e.g.</i> Wool/silk fibre Nylon/wool fibre Wool/polyurethane fibre Nylon/polyurethane fibre	Acid dyes
<i>AB blends, e.g.</i> Wool/acrylic fibre Wool/basic-dyeable polyester fibre Nylon/acrylic fibre Silk/acrylic fibre Polyurethane/acrylic fibre	Acid dye/basic dye
<i>AC blends, e.g.</i> Wool/cellulosic fibre Silk/cellulosic fibre Nylon/cellulosic fibre Polyurethane/cellulosic fibre	Acid dye/cellulosic dye
<i>CB blends, e.g.</i> Cellulosics/acrylic and modacrylic fibre	Cellulosic dye/basic dye
<i>CC blends, e.g.</i> Cellulosic/cellulosic fibre	Cellulosic dye
<i>DA blends, e.g.</i> Cellulose acetate/protein fibre Polyester/protein fibre	Disperse dye/acid dye
<i>DB blends, e.g.</i> Polyester/acrylic and modacrylic fibre Cellulose acetate and triacetate/acrylic fibre	Disperse dye/basic dye
<i>DC blends, e.g.</i> Cellulose acetate and triacetate/cellulosic fibre Polyester/cellulosic fibre	Disperse dye/cellulosic dye
<i>DD blends, e.g.</i> Cellulose acetate/triacetate fibre Cellulose acetate or triacetate/polyester	Disperse dyes

Cellulosic fibres, e.g. cotton, linen, viscose, and polynosic

Cellulosic dyes, e.g. reactive, direct, and vat

A: dyeable with acid dyes, B: dyeable with basic dyes,

C: dyeable with cellulosic dyes and D: dyeable with disperse dyes.

Additionally, selection of fibres along with their proportions in three-component blends, careful selection of dyes as well as dye combinations and dyeing conditions are very important for obtaining novel effects. Table 4.4 lists some useful ternary blends along with their dye combinations (Broadbent, 2001).

Table 4.4 Some useful ternary blends along with their proper dye combinations

Ternary blends	Dye of type combinations
<i>AAA blends</i>	
Nylon/wool/polyurethane	Acid dye
<i>AAB blends</i>	
Nylon/wool/acrylic	Acid/acid/basic dyes
Polyurethane/wool/basic-dyeable polyester	
<i>AAC blends</i>	
Nylon/wool/cotton or viscose	Acid/acid/cellulosic dyes
Nylon/polyurethane/cotton	
<i>CBA blends</i>	
Cotton/acrylic/nylon	Cellulosic/basic/acid dyes
<i>DAA blends</i>	
Cellulosic acetate or triacetate/nylon/wool	Disperse/acid/acid dyes
Polyester/nylon/wool	
Polyester/polyurethane/wool	
<i>DAC blends</i>	
Polyester/polyurethane/cotton	Disperse/acid/cellulosic dyes
Polyester/nylon/cotton or viscose	
Cellulose acetate/wool/linen	
<i>DBA blends</i>	
Polyester/acrylic/wool	Disperse/basic/acid dyes
<i>DBC blends</i>	
Polyester/acrylic/cotton or viscose	Disperse/basic/cellulosic dyes
<i>DDA blends</i>	
Cellulose acetate/polyester/nylon	Disperse/disperse/acid dyes
<i>DDC blends</i>	
Cellulose triacetate/polyester/cotton or viscose	Disperse/disperse/cellulosic dyes

Cellulosic dyes, e.g. reactive, direct, and vat

A: dyeable with acid dyes, B: dyeable with basic dyes,

C: dyeable with cellulosic dyes and D: dyeable with disperse dyes.

4.4 Main dyeing methods

The dyeing process can be carried out at different stages of textile material processing, i.e. staple fibre, yarn, fabric and piece. Dyeing machineries can be classified accordingly (Bellini *et al.*, 2002; Chaudhury, 2006; Nair and Pandian, 2008).

4.4.1 Type of textile material to be processed

- (i) Loose-stock dyeing machine for fibres.
- (ii) Hank/package/rope dyeing machines for yarns.
- (iii) Jigger/winch/jet/beam/padding mangle dyeing machines for fabrics.
- (iv) Rotary drum/side paddle for dyeing garments.

4.4.2 Processing methods

- (i) Discontinuous method; batchwise in rope form (winch, jet) or in open width (jigger) (Anis and Eren, 2003; Hyde, 1998; Moorhouse, 1996; Yang and Li, 2000).
- (ii) Semi-continuous systems.
- (iii) Continuous systems for high production.

The most popular sequences for semi-continuous range for fabric dyeing are:

Pad → cold batch → wash

Pad → preheating → hot batch → wash

Pad → dry → jigger development

The most popular sequence for continuous pad-steam range for fabric dyeing is:

Pad → dry → pad → steam fixation → wash

On the other hand, thermosol dyeing of polyester-containing fabrics involves the following steps:

Padding → pre-drying (using IR-pre-heater to avoid migration) → final drying (using steam cylinders) → dye fixation at 200–220°C for 30–60 s → washing.

4.4.3 Operating principles

- (i) Dyebath circulation systems
- (ii) Textile material moving systems
- (iii) Both dyebath circulation and textile material moving systems.

4.4.4 Process conditions

Closed (high pressure/high temperature) or open systems according to the type of material and the process to be carried out.

4.4.5 Selection of dyeing methods

Factors affecting the choice of dyeing methods, for particular blends to guarantee best dyeings involve (Aspland, 1997; Broadbent, 2001):

- Minimum use of natural resources as well as chemical consumptions, i.e. minimum pollution load.

- The demanded colour effects and fastness properties of the resultant dyeings.
- The stability of the obtained dyeings for subsequent finishing processes.
- Impact of type of dye as well as dyeing equipments, i.e. batch, semi-continuous and/or continuous ranges (Nair and Pandian, 2008).
- Economical and environmental costs of the overall dyeing process (Shore, 1981).

4.4.6 Selection of dyeing machineries

For proper selection of dyeing machineries, it is necessary to take into consideration (Bellini *et al.*, 2002; Nair and Pandian, 2008):

- Protection of the textile material
- Uniform penetration, level dyeing, higher build up, and maximum dye fixation
- Right First Time dyeings and reproducibility
- Environmental and economical aspects.

4.4.7 Dye selection and dyeing methods for some of the most important textile blends

Blends dyeing is a big challenge due to the differences in: nature of the blend components, dye substantivity, dyeing conditions, type of dyeing auxiliaries used as well as dyeing process, i.e. batch, semi-continuous and continuous dyeing. On the other hand, as mentioned before, classification of the textile fibres based on dye substantivity can be categorised into four principal groups, namely (Aspland, 1997):

- (i) Group A: Acid and pre-metallised acid dyes for dyeing wool, silk, nylon and polyurethane component via ionic interaction, and non-polar van der Waals forces (Doughty, 1986; Kue and Fang, 2006; Zhao *et al.*, 2004).
- (ii) Group B: Basic dyes for acrylics and modacrylics, cationic dyeable polyesters via formation of electrostatic (Coulombic) bonds (Holme, 2002; Kuo and Fang, 2006).
- (iii) Group C: Cellulosic dyes, e.g. reactive, direct, vat, sulphur, etc. via formation of physical and/or covalent bonds (Aspland, 1993; Bone, 2001; Carlough and Meszaros, 1989; Chao *et al.*, 1998; Shukla *et al.*, 1998).
- (iv) Group D: Disperse dyes for polyester, cellulose acetate, nylon and polyurethanes via hydrophobic bonding (Afifi and Sayed, 1997; Aspland, 1993; Carlough and Meszaros, 1989; Choi and Towns, 2001; Doran, 1999; Holme, 2002; Hook, 1992; Qian and Song, 2007).

As far as blends dyeing is concerned, the most demanding task is to get solid shades, regardless of the blend components. Some of the most commonly used fibre blends, and the selection of proper dyes, and methods for dyeing these representative fibre blends are listed in Table 4.5.

4.5 Future trends

Dye-houses have been forced to become increasingly innovative in order to develop their dyeing processes and products in order to: obtain high-quality dyeings with novel effects, reduce effluent loads thereby reducing environmental impact of dyeing process, respond to requirements and remain competitive in a market where profit margins are becoming tighter. During the last few years, considerable efforts have been made to increase innovation in the dyeing business. For blends dyeing, the major developments have been centred upon the development of fibre blends and enhancing the dyeability of fibre blends.

4.5.1 Development of fibre blends

- Introduction of high performance fibre using advanced science and technology (S&T) (Bide, 2009; Hongu *et al.*, 2005; McIntyre, 2005).
- Introduction of biodegradable fibres.
- Introduction of highly functional nano-structured fibres.
- Development of synthetic fibres for replacement of natural fibres.
- Preparation of polysaccharide-based polymer blends with natural and synthetic polymers using a solid-phase blending method (Rogovina and Vikhoreva, 2006).
- Production of sustainable fibres and how these fibres are subsequently processed such as organic cotton, bamboo, lyocell, polylactide acid fibre and organic wool.

There is still a clear need for further technical improvement in fibres blending in order to obtain developed/uniform yarns from different fibre types for producing blend fabrics with superior physicomechanical and dyeing properties taking into consideration both the economical and ecological aspects together with customer requirements.

4.5.2 Enhancing dyeability of fibre blends

Research and development efforts will and indeed are being made to enhance dyeability of textile blends:

Table 4.5 Dye selection and processes for some representative fibre blends

Fibre blends	Dye selection	Dyeing method	Colour effect
1. AA blends Polyamide/wool	Acid and metal complex dye (with anionic retarder)	Single class/exhaustion (levelling acid dyes or neutral pH metal complex)	Solid
Wool/polyurethane	Milling acid or 1:2 metal complex dyes (with retarder to control uptake)	Single class/exhaustion	Solid
2. AB blends Wool/modacrylic	Pre-metallised or milling acid Acid dyes/basic dyes (with a non-ionic anti-precipitant)	One bath/exhaustion	Solid or contrast
Wool/basic-dyeable polyester	Pre-metallised or milling acid dyes Acid dyes and basic dyes (with a non-ionic anti-precipitant)	Single class (at pH 6–7) One bath	Polyester – reserve, i.e. to be left white Contrast
Polyamide/acrylic	Levelling acid or 1:1 metal complex dyes/basic dyes (with a non-ionic anti-precipitant)		
3. AC blends Wool/cotton	Basic dyes pH 4–5 → pre-metallised dyes at appropriate pH	One-bath (pale shades) Two stages (full depth of shades)	Solid or contrast
Chlorinated wool/cotton	Acid dyes/low-sulphonated direct dyes	One-bath/exhaustion	Solid
Wool/viscose	Acid dyes/direct dyes (with non-ionic retarder)	One-bath/exhaustion	Solid
Wool/linen	Milling acid dyes → direct dyes	One-bath/exhaustion	Solid or contrast
Polyamide/cellulosic fibres	Milling acid dyes → reactive dyes Reactive dyes at pH 4–5 → salt and alkali	Two stages/exhaustion	Solid
	Pre-metallised or milling acid dyes/salt-controllable direct dyes	Single class/exhaustion One-bath/exhaustion	Solid Solid

Polyurethane/cotton	Pre-metallised or milling acid dyes/ direct dyes at pH 8	One-bath/exhaustion	Solid
Polyamide/cellulosic fibres	Pre-metallised or milling acid dyes/ salt-controllable direct dyes	Pad-dry-steam (continuous)	Solid
	Selected pre-metallised or milling acid dyes/reactive dyes	Pad-dry-thermofix-acid shock (continuous)	Solid
	Selected 1:2 metal complex dyes then vat dyes	Pad-dry-steam, Pad-dry-chemical pad-steam (continuous)	Solid
4. AD blends			
Wool/polyester	Selected acid dyes/disperse dyes (at pH 5–6, with carrier)	One-bath/exhaustion (pale-medium shades)	Solid
5. CB blends			
Cotton/basic-dyeable polyester	Direct dyes/basic dyes (with anti- precipitant)	One-bath at 120°C/exhaustion	Solid or contrast
Cellulosic/acrylic	Direct dyes/migrated basic dyes (with anti-precipitant)	One-bath/exhaustion	Solid or contrast
	Basic dyes at the boil → vat dyes at 50°C	Two-bath/exhaustion	Solid or contrast
	Basic dyes → vat dyes	Pad-dry-steam, Pad-dry-chemical pad- steam	Solid
6. CC blends	Basic dye → reactive dyes	Pad-dry-steam, Pad-dry-steam	Solid
Cotton/linen	Direct or vat dyes		
Mercerised cotton/viscose	Direct dyes (low salt, at the boil)	One-bath/exhaustion	Solid or shadow
Cotton/polynosic	Selected vat dyes at 50°C	One-bath/exhaustion	Solid
Cotton/lyocell	Selected highly reactive dyes	Pad-batch technique (continuous)	Solid
Viscose/polynosic	Direct, reactive or vat dyes	One-bath/exhaustion	Solid or shadow
Viscose/lyocell			
7. CD blends			
Cellulosic/polyester	Selected reactive/disperse dyes	Inverse dyeing (cellulosic first) on beam	Solid (pale shades)

(Continued)

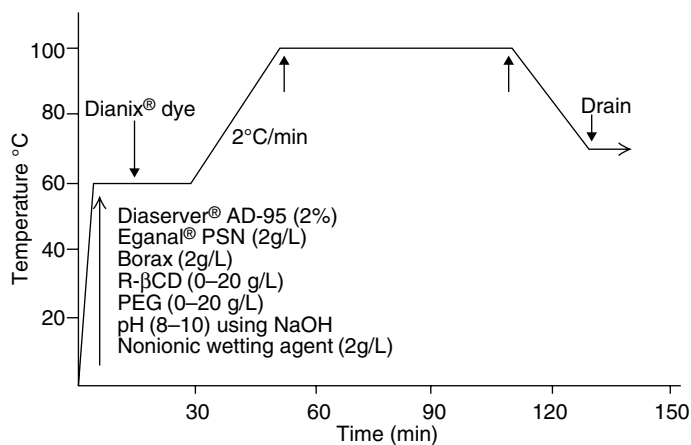
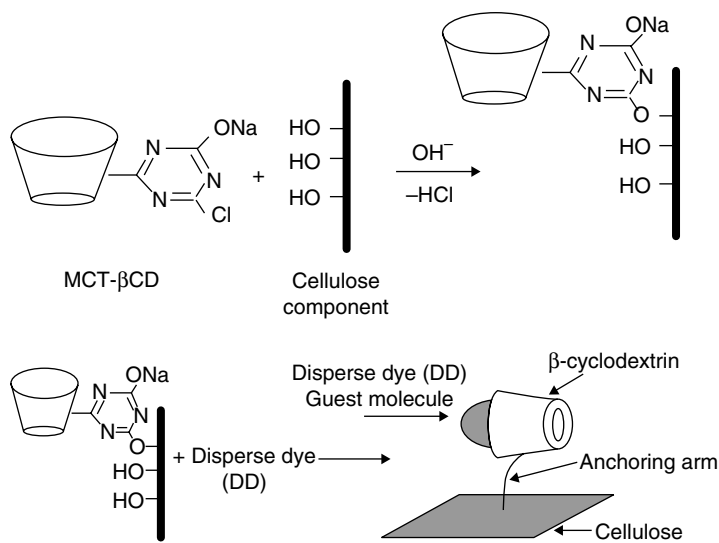
Table 4.5 Continued

Fibre blends	Dye selection	Dyeing method	Colour effect
8. DA blends Polyester/wool	Selected disperse dyes/selected 1:2 metal complex dyes	One-bath at 105°C (with carrier)/exhaustion Two-bath (disperse dyeing at 120°C → metal complex or milling acid dyes at the boil)	Solid Solid
Triacetate/wool	Selected disperse dyes/milling acid dyes	One-bath at the boil (with ester carrier)	Solid
Triacetate/nylon	Disperse dyes (at 105°C) → 1:2 metal complex (at the boil)	Two-bath (full depths)	Solid
Polyester/nylon	Acid dyes at neutral pH at 70°C → intermediate energy disperse dyes at 120°C	Two-batch (darker hue)	Solid or contrast
9. DB blends Polyester/acrylic	Disperse/basic dyes (with non-ionic carrier and anti-precipitant)	One-bath	Solid or contrast
	Disperse dyes at 120°C → basic dyes (with cationic retarder)	Two-stage	Solid or contrast
Acetate/acrylic	Basic dyes at the boil (with cationic retarder) → disperse dyes at 80°C	Two-bath (full depths)	Solid
10. DC blends Polyester/cellulosic	Disperse/reactive, direct, vat or sulphur	One or two bath/exhaustion (beam, Jet, high temperature winch or jigger)	Solid
	Selected disperse dyes/highly reactive dyes (with NaHCO ₃ + urea)	Pad-dry-themofix (continuous)	Solid
	Disperse dyes → then highly reactive dyes	Pad-dry-themofix-pad-batch (continuous)	Solid
	Vinyl sulphone dyes → disperse dyes at 130°C	Pad-batch-beam or jet (continuous)	Solid
	Disperse dye → then Low-reactivity dyes	Pad-dry-themofix-pad-steam (continuous)	Solid
	Selected vat dyes, or Solubilised sulphur dyes		

Acetate/cellulosic	Low energy disperse dyes/salt-controllable direct dyes	One-bath at pH 6–7 and 80°C/ exhaustion	Solid
Triacetate/cellulosic	Disperse dyes at 120°C → direct dyes at 90°C	Two-stage/exhaustion	Solid or contrast
11. Ternary blends Nylon/wool/polyurethane (AAA)	1:2 metal complex dyes (with an appropriate retarding and levelling agent)	Single class/exhaustion	Solid
Polyurethane/wool/basic-dyeable polyester (AAB)	Basic dyes with anionic retarder → neutral-dyeing acid dyes	Two stage/exhaustion	Solid
Nylon/wool/cellulosic (AAC)	Selected 1:2 metal complex or milling acid dyes and salt-controllable direct dyes with Syntan (as a retarding agent)	One-bath under neutral conditions/ exhaustion	Solid
Polyester/nylon/wool (DAA)	Disperse dyes and 1:2 metal complex or milling acid dyes with Syntan	One-bath (pale-medium shades), or two-bath method (disperse dyeing of polyester → reduction clearing → anionic dyeing of nylon and wool)	Solid
Acetate/wool/viscose (DAC)	Low energy disperse dyes at 80°C → direct dyes and neutral-dyeing acid dye	Two-bath method (disperse dyeing of acetate → reduction clearing → direct and neutral – acid dyeing)	Solid
Triacetate/polyester/viscose (DDC)	Intermediate energy disperse dyes and selected direct dyes at 120°C	One-bath method/exhaustion	Solid

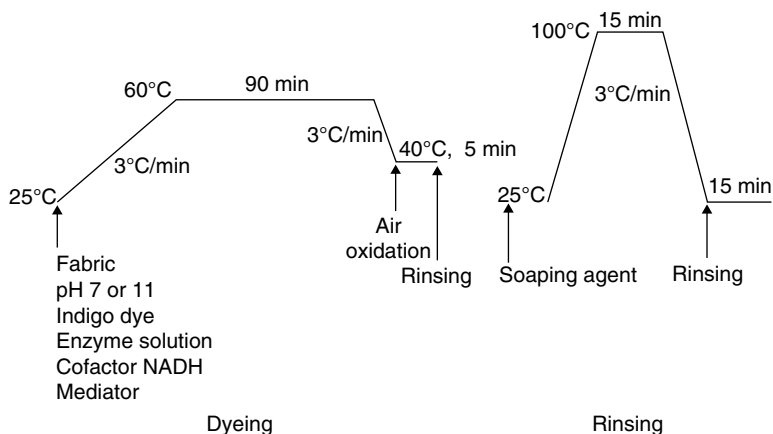
Source: Adapted from Shore, 1998.

- Plasma and laser treatments, as clean technologies, have been used to modify both the surface and dyeing properties of textile fibres, e.g. polyester, polyamides, polyolefin, wool, flax, etc. (El-Zawahry *et al.*, 2006; Ibrahim *et al.*, 2008; McIntyre, 2005; Park *et al.*, 2008; Yip *et al.*, 2002).
- Surface modification of silk fibres using chitosan and pre-treatment of polyester/cotton fabrics using chitin biopolymers have been reported as enhancing their dyeability with acid dyes and disperse/reactive dyestuffs in one bath respectively (Davaranah *et al.*, 2009; Najafi *et al.*, 2008).
- Incorporation of certain additives such as α -cyclodextrin in dyeing formulation of polyamide/wool fibre blend with one class of dye, i.e. acid dyes, and high boiling swelling agent, i.e. polyethylene glycol, in single stage dyeing of polyester/cotton blends with disperse dyes (Chalaya and Safonov, 2007; Sivakkumar, 2008).
- A novel approach for union disperse dyeing and ultra-violet protecting of cotton/polyester blend using monochlorotriazine β -cyclodextrin (MCT- β -CD) and alkali-stable disperse dyes has been reported (see Fig. 4.2) (Ibrahim *et al.*, 2010).
- Permanent modification of the cotton component of a blend by using hydrophobic aromatic compounds, e.g. cyclohexyl carbodiimide, benzoyl chloride to allow one-bath dyeing of polyester/cotton blends either with disperse dyes or with reactive disperse dyes (Lewis and Broadbent, 1997; Saus *et al.*, 1993).
- Alkaline one-step disperse/reactive dyeing of polyester/cotton blends, using conventional reactive disperse dyes, have been used to achieve substantial savings in materials, water, energy and production time as well as a reduction in environmental impact (Eren and Anis, 2004, 2005; Ibrahim *et al.*, 2003; Youssef *et al.*, 2008).
- Enzymatic treatments have been evaluated for enhancing the hydrophilicity as well as dyeability of textile fibres (Paulo and Gubtiz, 2003). On the other hand, substitution of sodium dithionite in indigo dyeing of both polyamide 6 and polyamide 6,6 use of NADH (β -nicotinamide adenine dinucleotide disodium salt)-dependent reductases from *Bacillus subtilis*, in the presence of mediator 1,8-dihydrox 9,10 anthraquinone, as an ecologically friendly reducing agent, and successful reuse of enzyme have been reported (see Fig. 4.3) (Bozic *et al.*, 2009).
- Application of supercritical carbon dioxide dyeing technology, as an eco-friendly/alternative dyeing medium, has been developed to enhance the dyeability of natural and synthetic textiles with disperse reactive dyes (Cid *et al.*, 2007; Kraan *et al.*, 2007; Schmidt *et al.*, 2003). However, the high cost of equipment has reduced the financial viability of this process.



4.2 Mechanism of modification of cellulose component and dyeing profile of cotton/polyester blend (Adapted from: Ibrahim *et al.*, 2010).

- An environmentally safe alternative to the hazardous textiles auxiliaries for disperse dyeing of polyester and nylon, dyeing of wool, application of metal complex dyes as well as for dyeing of polyester–wool blends have been reported (Christie, 2007).
- Maximising exhaustion, fixation and wash-off of dyes, using zero or minimum amount of salt as well as dyebath reuse have been evaluated showing that there is no adverse affect on the product quality and

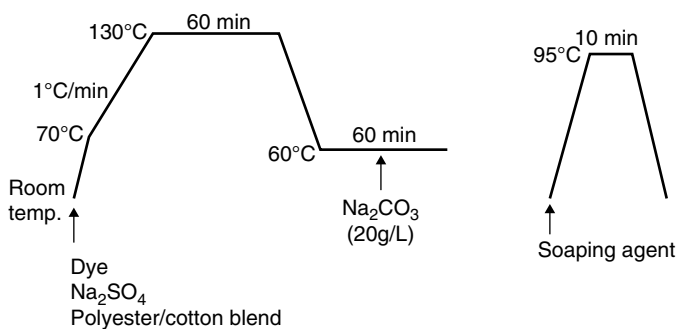
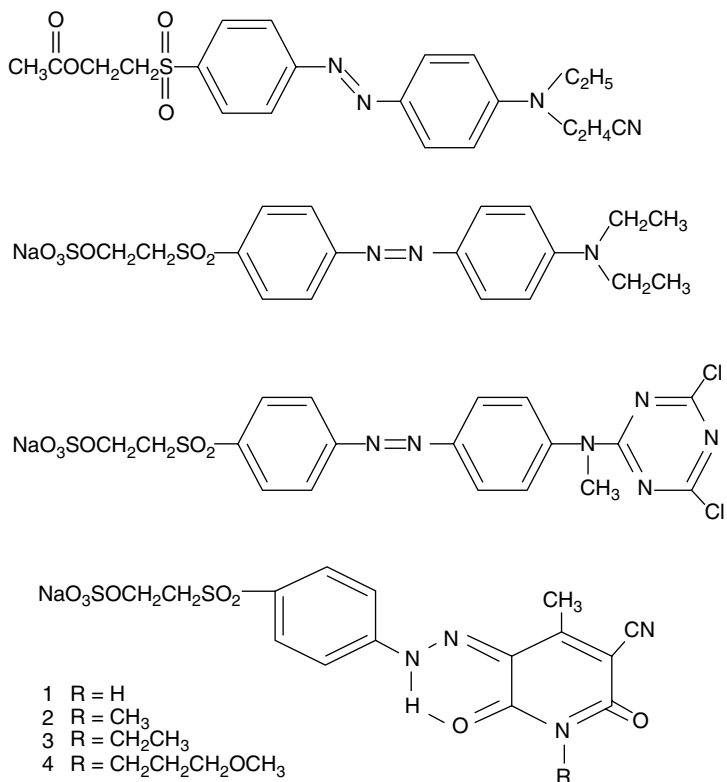


4.3 Mediated enzymatic indigo dyeing and soaping processes (Adapted from Bozic *et al.*, 2009).

reproducibility and also reduce the pollution load of the dye-house effluent (Christie, 2007).

- Development of universal dyes, i.e. reactive disperse dyes which have affinity for fibres of different chemical compositions to streamline manufacturing and to contribute to one-bath blend dyeing, e.g. polyester/cotton, wool/polyester, silk/polyester, silk/nylon, cotton/acrylic (see Fig. 4.4) (Bae *et al.*, 2006; Lee *et al.*, 2002, 2003; Schmidt *et al.*, 2003).
- Micro-encapsulated disperse dyes have been prepared, using disperse dyes as the core material and diphenylmethane-4,4'-diisocyanate as the wall-former of the capsule, characterised and utilised in dyeing PET at high temperature without the need for reduction clear after dyeing. Research has shown that dyeings obtained using this method were similar to those dyed using the standard disperse dyeing method. Following dyeing the polyurea microcapsules are separated from the dyebath so that the spent dyebath can be recovered and reused (Yi *et al.*, 2005).
- Nano-disperse dyes have been prepared using corresponding oil/water nano-emulsions, sodium laurylsulphate/carprylic triglyceride, under continuous ultrasound treatment. It was observed that the micro fibre exhibited higher K/S values than those of regular polyester, i.e. a higher dyeing efficiency on the ultra micro fibre polyester (Choi and Kang, 2006).

However, due to technical and/or economical reasons some of the aforementioned approaches are still in the development stage. It is not possible to speculate about the future of these options until they have been implemented on industrial scale by dye-houses.



4.4 Structures of some universal dyes and their dyeing profile
(Adapted from: Bae *et al.*, 2006; Lee *et al.*, 2002, 2003).

4.6 Sources of further information and advice

For a comprehensive and deeper insight into the scientific and technical aspects of blends dyeing, the following lists of information sources are recommended.

Articles

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www.alliance-mt.com
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 www.thiesmachine.com

Technical and safety data sheets are other useful sources of further information.

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Colourants and dyes for the cosmetics industry

R. J. W. HEFFORD, Independent Cosmetic Advice Ltd, UK

Abstract: This chapter discusses the use of colourants and dyes in the cosmetics industry. The focus is on the situation in the EU but the US situation is also considered. The technology is confused by the regulations and nomenclature governing this area especially in the EU. The area is spilt into two parts: those dyes used to colour the hair and those which are not. Direct dyes are used in both areas and oxidative systems are also used to colour the hair. The technology, chemistry and regulation of these types of colouring systems are discussed. A wide range of cosmetics utilise colourants and dyes and these are considered. Finally future trends are considered for colourants and dyes and the question of how regulation is likely to dominate future developments is considered.

Key words: colourant, dye, cosmetics, oxidative, direct, regulation, EU, USA, directive

5.1 Introduction

This chapter gives an introduction to the use of colourants and dyes in the cosmetics industry. A summary of the contents and the key issues in the area are given in this first section of the chapter.

Although the science behind colourants and dyes is consistent across the world unfortunately the regulations which deal with their use in cosmetics are not. This chapter has been written generally in relation to the EU cosmetics regulations as they are (and envisaged) at the time of publication; however, it also considers the regulatory position in the USA but does not consider the Japanese market in any depth. Unfortunately it is the nature of cosmetic regulation in the EU to be constantly changing and details should always be checked before any commitments are made. It is due to the nature of the EU (as well as US) regulations that it is important to draw a distinction between (cosmetic) colourants and (hair) dyes. Thus the EU and US regulations concerning colourants and hair dyes are dealt within the second section of this chapter along with some necessary definitions. Safety and toxicology issues, and hence regulation, are perhaps the most important issues driving the use and development of coloured materials in cosmetics at the current time and will continue to do so.

The third section in this chapter deals with the types of chemicals that are used as colourants and hair dyes. In general colourants tend to be materials

which do not easily penetrate the skin or hair. This is achieved by molecular size, as well as by chemical properties, or by a lack of water solubility. Hair dye molecules tend to be smaller and soluble (in the product); their organic molecules are (in the majority of cases) intended to penetrate the hair (and thus potentially the skin) to some degree. These hair dyes may be uncoloured initially and converted into dyes by an oxidation reaction. Alternatively they may be non-reactive to oxygen and exhibit colour prior to application. This section also discusses the dyes formed and the reactions occurring during the oxidation process. This section also highlights the issue of the use of synthetic versus naturally derived materials. The decision of the manufacturer and the consumer between whether to use natural or synthetic materials is not one that is necessarily made on a logical basis. Considerations such as sustainability and the preference for organic and 'non-chemical' materials have also become important in cosmetics where the more emotional aspects of raw material choice tend to be important.

The fourth section in the chapter deals with the types of cosmetics in which colourants and dyes may be used. Although the description of product types can be made relatively simple the 'creativity' of marketing personnel has complicated this to a great extent with the invention of a wide range of product names. The main issues when considering product formulation are stability and the effectiveness of the colourant or dye at delivering the desired function.

Future trends within colourants and dyes are considered in the fifth section and this is often dominated by safety and regulatory considerations within the cosmetics industry. A great deal of work has been disclosed over recent years through the patent literature and yet little of this actually arrives on the market. The tendency over the last years has been the loss of materials from cosmetic usage rather than their introduction. A key issue is, therefore, whether current legislation is retarding innovation rather than encouraging it and is preventing the replacement of materials which might have 'sub-optimal' cosmetic properties.

5.2 Regulations and definitions

The cosmetics industry in the EU is currently regulated via the Cosmetics Directive which was first enacted in 1976 (Commission Directive 76/768/EEC) and has been subsequently modified by a number of Commission and Council Directives. Commission Directives are more numerous and add or delete materials from the various annexes within the Directive. Council Directives, which require a great deal more work, as well as passage through the European Parliament, are thus less numerous and alter the structure of the Directive itself. The latest version, and any later adapting Directives, is available through the website of the European Commission Enterprise and Industry DG (Enterprise A). The Cosmetics Directive instructs the Member

States of the EU (e.g. the UK, Germany and France) to enact legislation by a certain date and within the UK this is known as the Cosmetic Product (Safety) Regulations and there are a number of UK amendments which have yet to be consolidated within the main text. This UK Regulation is now the responsibility of the Department for Business Innovation and Skills (its name changed again recently and may have again before you read this) and the UK regulation can be seen on their website (BIS).

Legislation to change the Cosmetics Directive to an EU Regulation has passed through the EU process (in late 2009) and has been published in the Official Journal of the European Union (Europa a). This will, in principle, make cosmetics legislation more straightforward (for the legislators) and remove the need for a section of BIS (and thus help with the need to reduce public spending in the UK). The regulation will apply as law across the EU removing the need for redrafting in each Member State. The change is unlikely, however, to make compliance any easier for the people who manufacture and market cosmetic products in the EU.

The Cosmetics Directive defines what is and what cannot be a cosmetic product within the EU. It also contains a set of annexes or lists (both negative, i.e. banned, and positive, i.e. allowed) of materials. Thus Annex 2 contains well over 1000 banned materials including materials that have been traditionally used as colourants and hair dyes (and still are in some other countries). Annex 3 is a list of allowed but restricted materials and Annex 4 is a list of 'colourants allowed for use in cosmetic products'. The Directive also envisages a positive list for 'colouring agents intended solely to colour hair' of (hair dyes); however this has yet to be created (as of 2011) and might not be so for a number of years. Thus under the definitions of the EU Cosmetics Directive colourants and hair dyes are treated as two different entities. When a positive list for hair dyes does occur in the EU it will be within the context of the new Cosmetics Regulation and it is foreseen that it will eventually form an additional part of Annex 4. Thus materials that can produce a colour either in a product or on the human body can fall, as defined in the EU, into two distinct categories:

1. Materials known as 'cosmetic colourants' which do everything else and are listed in Annex 4.
2. Materials designed to colour the hair known as 'hair dyes'.

When the Cosmetics Directive was created it was thought that certain materials with particular functions, e.g. colours and preservatives, were more dangerous than other types of raw materials and required particular attention, thus the annexes were created. To determine the safety of these 'higher priority' materials the EU Commission requested that safety dossiers were created (by 'industry') to support their use. The contents of these dossiers and their evaluation is controlled by an expert committee (of non-Commission

scientists) but under the control of DG Health and Consumers. This committee has had a number of titles over the years and is currently known as the Scientific Committee on Consumer Safety (SCCS) but has also been known as the 'SCCP' and the 'SCCNFP'. The results of the evaluation of the safety dossiers are published on the DG Health website (Health a) and these opinions are subsequently converted by DG Enterprise into regulation via Commission Directives.

5.2.1 EU cosmetic colourants

Cosmetic colourants are quite well defined in Annex 4 and fall into four regulatory divisions defined in the Directive as columns.

1. Colouring agents allowed in all cosmetic products.
2. As (1) except those intended to be applied in the vicinity of the eyes.
3. Allowed exclusively in products not intended to come into contact with the mucous membranes.
4. Only allowed in products in brief contact with the skin (i.e. rinse-off products).

These colourants are most often listed in the Directive by their Colour Index (C.I.) numbers (there are some exceptions) and the colourants are named on EU ingredient listings (as required by the Directive) in this way. All ingredients listed on EU packages must be identified by their designated INCI (International Nomenclature of Cosmetic Ingredients) name. A list of these names is now usefully available (in a database called CosIng although there is no guarantee that this is accurate) through the DG Enterprise and Industry website (Enterprise B). INCI names are controlled and issued by the PCPC (Personal Care Products Council); this is the cosmetics trade organisation of the USA which was formerly known as the CTFA (Cosmetic, Toiletry, and Fragrance Association). Cosmetic ingredients must also be listed on products intended for sale in the USA. However, not all ingredients are named in the same way in both areas with colourants and botanical extracts being notable examples and this leads to the necessity of dual labelling on products (as well as a degree of confusion) intended for both areas.

5.2.2 EU hair dyes

Hair dyes are currently less well defined within the EU regulatory framework. The situation may be summarised as follows.

- Some hair dyes are listed in Annex 2 and are thus banned for use as hair dyes in the EU. This now includes some materials which are allowed in the USA and elsewhere in the world.

- Some hair dyes are in Annex 3 Part 1 (fully allowed) and may be used within the parameters defined in the Directive which also includes labelling requirements.
- Others are in Annex 3 Part 2 (provisionally allowed). This part has a defined end-date which in recent years has been the subject of continuing extension. Materials pass from here either to Annex 3 Part 1 or into Annex 2.
- Materials which are in none of these Annexes may also be used as hair dyes in the EU at the present time; however, the user must be sure that the material and the product are safe for use. Thus in addition to all these Annexes in the EU regulations there is also the overriding requirement for a safety assessment to be carried out on every product by a suitably 'qualified' person. Once a hair dye positive list is created this section will vanish.
- Regardless of the regulatory situation of the dyes described above it is possible to get a good idea of which dyes will or will not eventually be on the positive list in the EU as the Commission publishes a list of 'supported' hair dyes which in mid-2010 contained 123 materials. These dyes have had safety dossiers supplied by industry and are expected to eventually have completed data supplied for them. This list is available through the appropriate website (Enterprise C).

Unlike colourants hair dyes are not listed by their C.I. numbers but by INCI names derived more closely from the original CTFA (sometimes trivial) nomenclature, e.g. paraphenylenediamine (PPD) and HC Blue No 2.

Thus for all the extensive EU legislation the situation with respect to hair dyes is not clear and is made less so by the problem of a lack of definition in the Directive for the word 'hair' (at least in English) as well as for the word 'dye'. The question as to what 'hair' is has not been answered unambiguously as yet as there is hair on various parts of the body: head, eyebrows, eyelashes, chest, pubic area and legs. Additionally how should a product that is intended to colour the hair temporarily be defined and should hair dyes or cosmetic colourants be used in this type of product? If the product type is defined by the longevity of the effect (i.e. does it wash off?) what happens if the colourant actually dyes hair (i.e. doesn't wash off) that is light and damaged? Generally materials which colour the hair temporarily are labelled with C.I. numbers thus implying that only colourants should be used for this purpose. The final test for any unclear application should always be a comprehensive safety assessment and the product should only be placed on the market if this has been (successfully) carried out.

The conversion of the EU Cosmetics Directive into a Regulation might help to clarify some of these difficulties but it might not. It is intended to place hair dyes into a further column in Annex 4 at some time in the future and this will create a positive list; however, the timing for this has not yet been defined.

5.2.3 US regulations

It is intended that cosmetics regulations will eventually become 'harmonised' across the world and the use of the INCI nomenclature and process was a good step towards this. However, there are still differences in the regulation and naming of materials which impart colour in cosmetics and these can be known as 'colour additives' in the USA. Perhaps the best place to find out about regulation in the USA is through the PCPC. They have a website (PCPC) and publish the *International Cosmetic Ingredient Dictionary and Handbook* (CTFA, 2006) as well as other useful publications regularly.

Somewhat similar to the EU a distinction does exist in the USA between 'coal tar' (synthetic organic) colourants used in hair dyes and all other colour additives. In the USA a cosmetic containing a colourant (except a coal tar hair dye) that is not approved by the FDA (Food and Drug Administration) is regarded as 'adulterated' and subject to regulatory action under the Food, Drug and Cosmetic Act. Colour additives approved for use in the USA fall into three sections.

1. Colour additives batch certified by the FDA
2. Colour additive lakes batch certified by the FDA
3. Colour additives exempt from batch certification by the FDA.

Each batch of an approved synthetic organic colourant must be tested and certified by the FDA as meeting the standards and specifications found in 21 CFR 74 (from the US code of Federal Regulations). Although some approved colourants are exempt from batch certification they still must meet a specification stated in the regulations. The names for these colourants may have a prefix (e.g. FD&C Blue 1) which indicates that the colourant is approved for use in foods, drugs and cosmetics.

An exception to this rule was made for 'coal tar' (synthetic organic) hair dyes, however, and the products in which these are used must display a defined set of cautions and warnings including the requirement for a pre-use patch test designed to determine if the user is sensitised to any ingredient in the product. Interestingly in the USA the term 'hair dye' does not include dyes intended to colour the eyelashes or eyebrows. Additionally colourants which might be used to colour the hair such as those derived from vegetables or metallic salts do not fall under this exclusion and require approval from the FDA prior to use.

Whereas the nomenclature for synthetic hair dyes in the US is generally identical to that used in the EU the naming for colourants is not. The names used are those defined by the FDA but can be used in an abbreviated form, see Table 5.1 for some examples.

Table 5.1 Examples of some water-soluble dyes with USA and EU nomenclature

Certified US/ INCI name	Uncertified US/ INCI name	C.I. number	INCI hair dye name	Type	EU Annex 4 column
(D&C) Red 33	Acid Red 33	17200	Acid Red 33	Az	1
(FD&C) Yellow 5	Acid Yellow 23	19140	Acid Yellow 23	Az	1
(FD&C) Blue 1	Acid Blue 9	42090	Acid Blue 9	T	1
(D&C) Red 28	Solvent Red 48	45410	Acid Red 92	X	1
(D&C) Green 5	Acid Green 25	61570	Acid Green 25	An	1
None	Acid Black 1	20470	Acid Black 1	DiAz	4

Az: Azo dye; T: Triphenylmethane; X: Xanthene; An: Anthraquinone; DiAz: Two azo functional groups.

5.3 Raw material types and chemistry

A wide range of different chemical types are used as colourants and as hair dyes. A few materials are used in both classifications. Materials used fall into the broad categories of organic and inorganic as well as from synthetic or natural sources.

5.3.1 Materials used as cosmetic colourants

Cosmetic colourants used in cosmetics fall into two broad categories: those which are soluble in the product and those which are insoluble. The following definitions are generally accepted within the cosmetics industry. For a good source of further information on this subject see Riley (2000).

- **Dyes:** Coloured materials which are soluble in the product formulation (these are usually water-based but could be oil-based). Some of these materials may also be used as hair dyes.
- **Pigments:** Coloured (or white) materials which are insoluble in the product formulation. This is a broad definition which also covers the more complicated materials described below.
- **Lakes:** Pigments made by depositing the aluminium or zirconium salt of a water-soluble dye onto a water-insoluble inorganic material. The definition of a lake can vary (by usage and geography) and care must be taken when considering this term.
- **Toners:** A pigment made by precipitating a water-insoluble metal ion salt of a water-soluble dye.
- **Pearls:** A material which gives a pearlescent or lustrous effect and may be coated with other materials to modify this effect.

- Extender/diluent/filler: A material that is added to (usually) a pigment during its manufacture to allow for batch variations in colour performance or to lower this to the desired level.

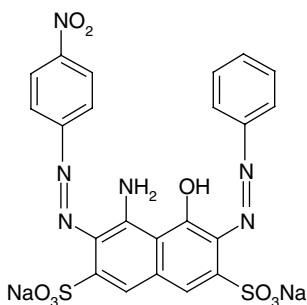
Dyes (which are soluble in the product) are generally used to colour products and are rarely used to colour the skin (see Section 5.4.1). These materials may be synthetically or naturally derived and are based on conjugated aromatic systems. Synthetic dyes are sometimes described under the (unfortunate) heading of 'coal tar dyes' after the original source of their starting materials.

The most important class of synthetic water-soluble dyes are the azo dyes which contain an $-N=N-$ chemical group (some may contain two of these groups). The water solubility is given by the inclusion of carboxylic acid or sulphonic acid groups usually substituted onto the aromatic functions. Other chemical types found in this type of dye include triphenylmethane, xanthene (substituted fluoresceins) and anthraquinone. For common examples of these dyes see Fig. 5.1 and Table 5.1. These dyes can suffer from poor light stability and may sometimes react with other materials (e.g. metal ions) in the product formulation. In addition they are usually pH sensitive, either changing colour at particular pH values (some have been commonly used as pH 'indicators') or may hydrolyse quickly at more extreme pH values.

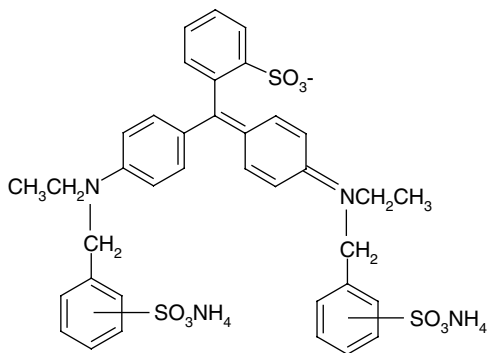
A small number of 'natural' dyes are listed in Annex 4 of the Cosmetics Directive and these include caramel, capsanthin/capsorubin, beetroot red and anthocyanins. These materials are becoming more popular with cosmetics consumers but they do suffer from poor stability and badly defined raw materials. Unfortunately it is generally true that these materials have an inferior performance to their synthetic counterparts.

At their simplest pigments are coloured materials which are insoluble in the product formulation and they may be organic (which can be quite bright) or inorganic (which can be relatively dull) in nature. Organic pigments can be very similar in structure to the dyes described above but without sufficient groups to render them soluble in common cosmetic materials. A good example is the monoazo colour C.I. 12085 (or D&C Red No. 36) (see Fig. 5.2). This pigment is insoluble in water and will not 'bleed' into aqueous products. It is also insoluble in oils, waxes and organic solvents but will bleed slightly into these.

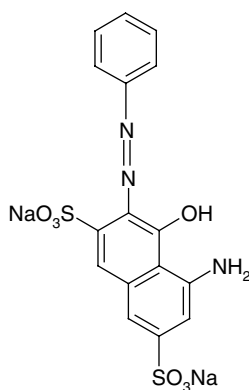
In the cosmetics industry true lakes are usually made by depositing the aluminium (or zirconium) salt of an FD&C soluble dye onto alumina (or other permitted substrate) and these are widely used in decorative cosmetics. In the EU the aluminium salt of any of dyes permitted in Annex 4 can be used so long as they fall into the appropriate category, i.e. generally those permitted around the eyes only. These lakes are stable in oils, waxes and aromatic solvents but can bleed in aqueous products. They can also break down



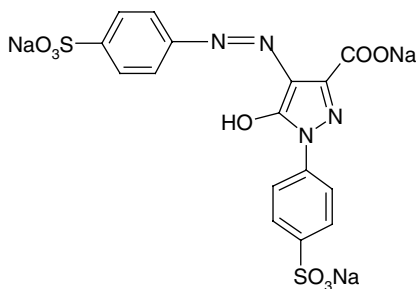
Acid Black 1/C.I. 20470



Acid Blue 9/C.I. 42090

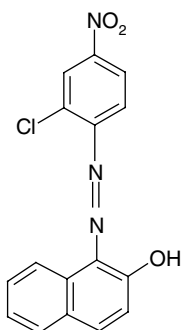


Acid Red 33/C.I. 17200

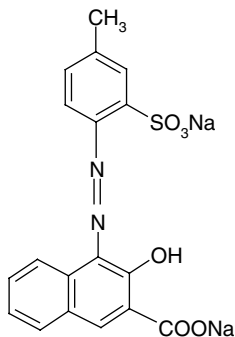


Acid Yellow 23/C.I. 19140

5.1 A selection of commonly used water-soluble synthetic dyes.



Red 36/C.I. 12085



Red 6/C.I. 15850

5.2 Some 'pigments' commonly used in decorative cosmetics.

in acid or alkali releasing the dye which is water soluble. Oddly the labelling of lakes in the EU does not require the cation to be mentioned, neither is necessary to include the nature of the substrate onto which it is deposited. However, in the USA the materials are designated with the word 'lake' after the name of the dye.

Toners are made by the precipitation of a (largely) insoluble calcium or barium salt of a dye containing acid groups. An example of this type of material is C.I. 15850 and its structure can be seen in Fig. 5.2. Within the C.I. nomenclature it is possible to identify the particular counter ion that is used to form the toner or lake, e.g. C.I. 15850:1 – the calcium salt or C.I. 15850:2 – the barium salt. As barium, strontium and zirconium salts are regulated (banned) elsewhere in the EU Cosmetics Directive these salts (of particular dyes only) are specifically indicated in Annex 4. C.I. 15850 is not very soluble in water (as the sodium salt) due to its structure. Its calcium and barium 'toners' are quite resistant to bleeding and (chemically) stable in alkali; however, they do bleed slightly in oils, waxes and organic solvents. They have good heat and light stability but will change colour at high and low pH.

A further large category of pigments is made up of inorganic materials which are superior to organic materials in terms of overall chemical stability (with the exception of reactivity at extremes of pH); however, in general the colours produced are duller. The most commonly used inorganic pigments are the iron oxides and there are three main colours – red, yellow and black – from which a large number of different natural looking flesh tones can be produced by mixing. These three materials have three different C.I. numbers, which are used as the INCI names in the EU, whilst in the USA these materials are all called 'iron oxides'. These are generally manufactured synthetically. Iron oxides do tend to be discoloured at low pH.

A second group of inorganic pigments is based on chromium oxides which tend to give green-based colours. A further set of materials is based upon complex sodium aluminium sulpho-silicates under the name 'ultramarines' which can produce colours ranging from blue and violet to pink as well as green. Regardless of colour these all have the same C.I. number which is used as the INCI name in the EU. These materials may often be coated in some way as they are susceptible to reaction with acid releasing hydrogen sulphide. A bright violet/purple colour is given by the pigment manganese violet (which is stable in acid but will decompose in neutral or alkaline products) and blues can be obtained by two forms of iron blue. The iron blues are also unstable in alkali and can be difficult to disperse.

A range of pigments exist which can be used to deliver a white, colourless or translucent effect are also permitted and these include titanium dioxide, zinc oxide, alumina hydrate and barium sulphate. The last is often used as a pigment extender. Titanium dioxide can be regarded as almost the perfect pigment as it has a very useful set of physical and chemical properties

being very resistant to most cosmetic environments. Both titanium dioxide and zinc oxide are also used for other purposes in cosmetics including use in sunscreen products. This raises a completely different set of difficulties which are made even more complex by the introduction of very small (or nano) particle sizes. That is the subject for another time and place.

An important aspect of all of these inorganic pigments is the levels of unacceptable (heavy) metals in the materials and these must be known and very carefully controlled. The barium, strontium and zirconium salts of the allowed organic dye molecules must also pass an insolubility test which is laid down in the Cosmetics Directive.

All the colourants described so far can be used to impart colour effects to a range of cosmetics. However, a range of additional and more complex materials also exist which can give more lustrous or 'pearlescent' effects. The first of these materials were derived from naturally occurring sources such as pearls themselves but these materials have become much less used due to cost and the fact that more modern manufactured materials can give much better and a wider range of effects. A brief description is given here and more detail can be obtained elsewhere (Riley, 2000).

An early synthetic pearlescent material that is still used in cosmetics is monocrystalline bismuth oxychloride. These materials are made by careful growing of BiOCl crystals which is a difficult process requiring much experience to obtain reproducible results. Additives are also required to obtain the desired 'lamellar' crystal structure. The low solubility of the solid material makes it acceptable for cosmetic use. These materials are often supplied dispersed in oil and their main drawback is a low light stability often requiring opaque packaging to exclude light completely.

A cosmetically 'ideal' pearlescent material would be lamellar titanium dioxide; however, this has resisted all attempts to be produced. A good alternative for this is to coat a flat material with a thin layer of titanium dioxide and an ideal material for this is mica which is naturally occurring, transparent, safe for use, cheap and chemically resistant. Once the mica powder is prepared from the mined material a layer of titanium dioxide is usually created by the hydrolysis of a titanium salt solution in the presence of the suspended mica. To create the 'best' surface a pre-treatment of tin oxide can be used on the mica which enables the titanium dioxide to deposit in the rutile, rather than the usual anatase form. Fortunately tin oxide is allowed as a colourant in both the EU and US. The effects created by these pearls are dependent upon the size of the mica particles and by the thickness of the surface layer. As the layer increases in thickness the perceived colour of the pearl changes to yellow/gold to copper/red then lilac followed by blue and then green. These materials are known as 'interference pearls'.

It is also possible to coat these particles with some of the inorganic pigments described previously if they have a sufficiently high refractive index. Iron oxides can be deposited onto the mica/titanium dioxide surface by careful hydrolysis of an iron salt in solution with the particle dispersion. In this way the colour of the iron oxide is amplified and it is possible to obtain a large range of mixed colours, e.g. red/violet and red/green. Inorganic pigments may also be used to coat mica particles in the absence of a titanium dioxide layer. In theory an almost infinite range of colour combinations can be produced. However, the production of red pearls is more difficult largely due to regulatory restrictions for use of some of the materials around the eyes.

The ability to coat colourant/particle surfaces is useful when attempting to produce physical properties which enhance a range of raw material functions such as the following.

- Physical stability within the product, e.g. lack of separation and clumping
- Ability to impart good 'bulk' properties, e.g. pressability in cakes of make-up
- Useful properties on the skin such as hydrophobicity (adhesion to the skin) and an 'elegant feel'.

One surface treatment used on particles is that of silicone and these materials can give a good and beneficial hydrophobicity to the material. The first and most commonly used silicone is dimethicone (INCI name) and these polymers come in a vast range of molecular sizes from small and volatile through to very large and waxy. Other useful surface treatments include amino acids, e.g. lysine, hydrogenated lecithin (sometimes with a polyacrylate), collagen and polytetrafluoroethylene (PTFE).

A more hydrophilic nature can be introduced to the particle by the use of dimethicone copolyols which are useful in dispersing and stabilising pigments in water-based systems. Many different surface treatments are possible and the choice depends upon the nature of the product base and the desired benefits.

5.3.2 Materials used as hair dyes

From a chemical viewpoint there are two general and distinct types of hair colouring product which use hair dyes and these are as follows.

- Oxidative systems which usually rely upon an added oxidising agent just prior to application or a very few products which rely upon aerial oxygen as the oxidant. These products contain essentially non-coloured dye precursors which react under oxidising conditions to form larger coloured dye molecules within the hair shaft (usually right into the centre of the

cortex) where they become trapped. This type of system can give long lasting and ‘permanent’ colouring effects with lightening of the hair colour or non-lightening colours which are designed to last only up to 28 washes (or sometimes less).

- Direct systems which contain coloured dye molecules that have already been formed and do not require subsequent reaction. In this type of system the dyes either diffuse some way into the hair (the cuticle and some of the cortex) or are strongly attached to the surface and give semi-permanent effects (lasts 6–8 washes) and possibly more temporary effects.

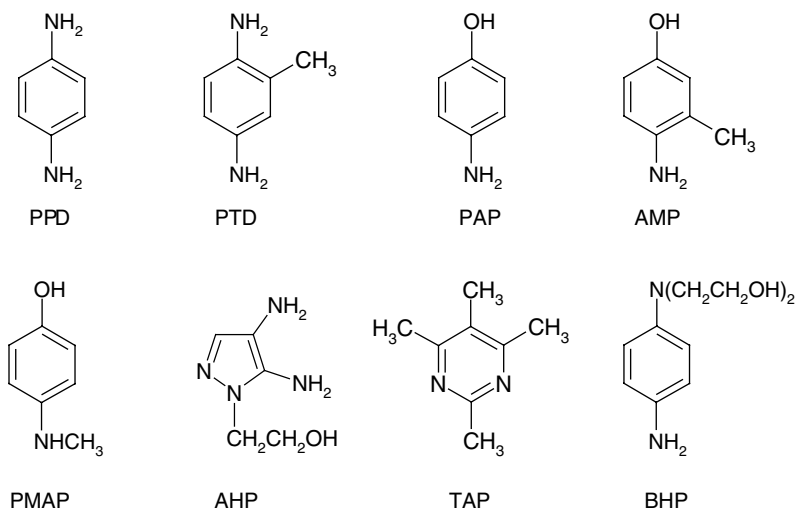
Oxidative systems

The chemistry of these hair dye materials (especially within the hair) is very complex and only a brief summary can be given here. For a more detailed review see Corbett (1998) and Zviak and Milléquant (2005). The first author, John Corbett, worked for Clairol for many years and this reference tends to give a US/Clairol view of hair colouring. Charles Zviak, now deceased, occupied a similar role in L’Oreal and this reference gives a more French/L’Oreal view of the subject. A good and useful summary of the structure of the hair is given by Swift (1997) who worked for many years at Unilever Research.

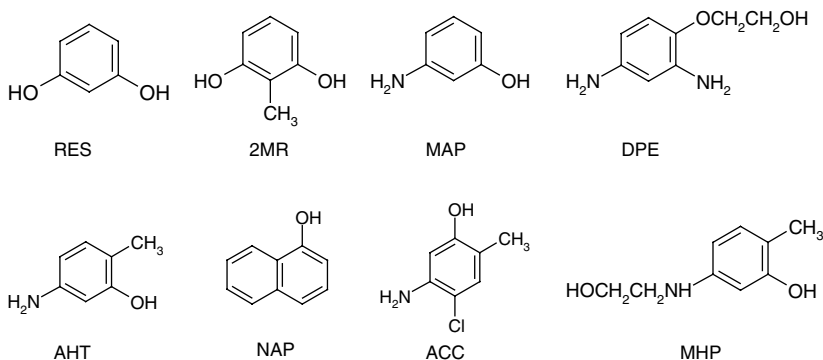
The types of chemical used in oxidative hair colouring systems were discovered in the nineteenth century and the first of these which was linked to colouring natural fibres and materials was PPD. This is the INCI name for 1,4-diaminobenzene and the INCI names for dyes will generally be used in this text. PPD still remains the most important, cost effective and widely used oxidative hair dye in the world; unfortunately it also remains the most controversial.

When oxidised in isolation PPD is believed to form a very dark compound (often known as Bandrowski’s base) and this has been used as the basis for black and very dark hair dyes. However, this is (in general) no longer considered safe for use in isolation (in Western countries) for a number of toxicological related reasons. It is recognised practice, therefore (in the EU at least), to use PPD in combination with other materials which react with it to form coloured compounds. An example of this is resorcinol (RES) which with PPD, and an oxidising agent, will give a muddy green/brown coloured dye.

The reaction of PPD with an oxidising agent [O] starts the colour forming reaction with the creation of p-benzoquinonediimine (PBD) and this class of dye precursors is known as ‘primary intermediates’ (PIs) or ‘oxidation bases’. These PIs are generally either para or ortho substituted diaminobenzene or aminophenol compounds which may be substituted on the amino nitrogen or sometimes on the ring itself. A range of more commonly used PIs are given in Fig. 5.3. The PBD is believed to react rapidly with the colour forming compounds, which are usually known as couplers or colour



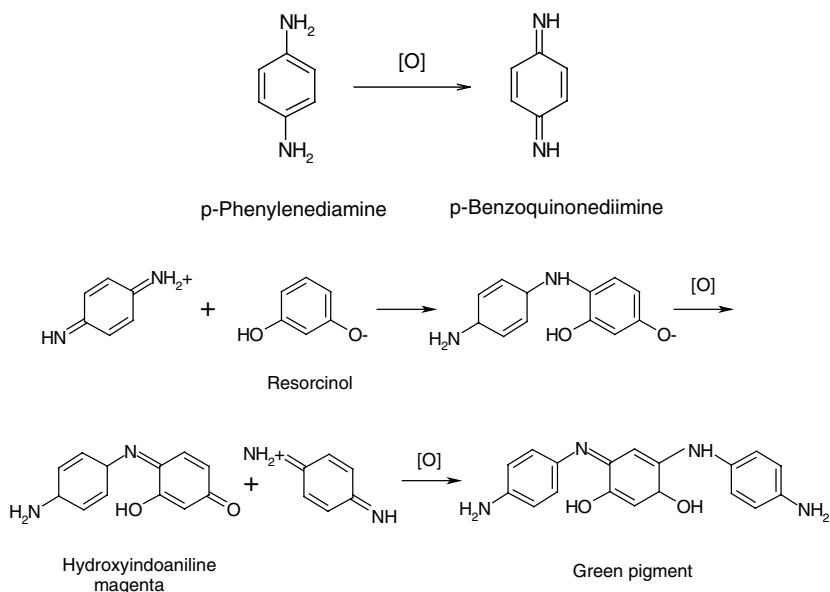
5.3 A selection of more commonly used PIs.



5.4 A selection of more commonly used couplers.

modifiers (Cs), and these materials are usually meta substituted amino and/or hydroxyl containing aromatic species. A range of more commonly used Cs is given in Fig. 5.4. A brief reaction scheme involving PPD and RES is given in Fig. 5.5.

A large range of colours are possible when combining a number of different PIs and Cs and it is possible to obtain quite good 'natural' hair colours with four of these materials although an average of perhaps six or more dye precursors is often used. When using one PI it is possible to obtain a range of colours although this can be limited and it is often the practice to use additional PIs to obtain the full range of possible effects. An idea of what might be achieved is given in Tables 5.2 and 5.3. Because there are a large



5.5 The reaction between PPD and RES in the presence of an oxidising agent under alkaline conditions.

Table 5.2 Some oxidative dye couplers and colours when reacted with PPD

Code	INCI name	Comments on colour with PPD
RES	Resorcinol	Green brown good basis for grey cover colours
2MR	2-Methylresorcinol	Introduces more of a yellow tone compared to RES
MAP	m-Aminophenol	Purplish/pink brown used as a 'balance' against RES
DPE	2, 4-Diaminophenoxyethanol	Dark bluish purple developed and used by L'Oreal
AHT	4-Amino-2-hydroxytoluene	Similar to MAP but more towards red
NAP	1-Naphthol	Greyish purple used by Clairol with BHT to give a purplish/blue
ACC	5-Amino-4-chloro-o-cresol	Gives a clearer purple colour
MHP	2-Methyl-5-hydroxyethylaminophenol	Similar to MAP but gives a more orange colour with PAP

number of combinations a full description cannot be given here but Corbett (1998) and Zviak and Milléquant (2005), as well as information from hair dye suppliers, should be consulted.

Although PPD is allowed by regulation for use in hair colouring products across the world it is particularly disliked in Germany and also by some other

Table 5.3 Some oxidative dye PIs

Code	INCI name	Comments
PPD	1, 4-Paraphenylenediamine	Dark colours and cost effective creation of colour depth
PTD	Toluene-2, 5-diamine	Alternative to PPD preferred in Germanic countries
PAP	p-Aminophenol	Used when 'redder'/warmer shades are desired
AMP	4-Amino-m-cresol	Less effective replacement for PAP used by Germanic manufacturers
PMAP	p-Methylaminophenol sulphate	Lighter shades than PAP
AHP	1-Hydroethyl-4, 5-diaminopyrazole sulphate	Used to give brighter red shades. Subject of (Wella) patents check status
TAP	2,4,5,6-Tetraaminopyrimidine	Interesting dye that is becoming more commonly available
BHP	N,N-Bis(2-hydroxyethyl)-p-phenylenediamine sulphate	Originally subject of a Clairol patent useful in silver shades

countries in Northern Europe. In Germany PPD is replaced by toluene-2, 5-diamine (PTD or TDS) which is most often available as the sulphate salt. For this material the alternative name paratoluenediamine was not adopted for labelling purposes and this highlights the illogical nature of this area. PTD/TDS has a higher molecular weight than PPD and is less effective (on a molar concentration basis at creating dark colours) and is thus less cost effective. In general this material is used by companies based in Germany and those who wish to sell their products in Northern Europe. PTD was also discovered in the nineteenth century as a way of avoiding the original PPD patent so things have not changed a great deal.

Perhaps the third most used PI is p-aminophenol (PAP). This dye is used when a more reddish, perhaps auburn, tone is required within the shade and is usually used in combination with PPD or PTD as it does not produce the depth of colour or grey coverage of these two materials. PAP is also disliked in Germany as it has been classified under the EU chemical legislation as a class 2B mutagen. This classification requires an immediate consideration by the SCCS and currently any material classified as a class 1 or 2A CMR will receive an automatic ban under the Cosmetics Directive. PAP is allowed currently in the EU but although it has not been banned, it has not yet been positively regulated either. It is unlikely to suffer a ban in cosmetics as its metabolic pathway in the body is closely linked to that of the painkiller paracetamol.

Within the Cosmetics Directive dye precursors which are not coloured and react with oxygen are described as 'substances in non-oxidative hair dye

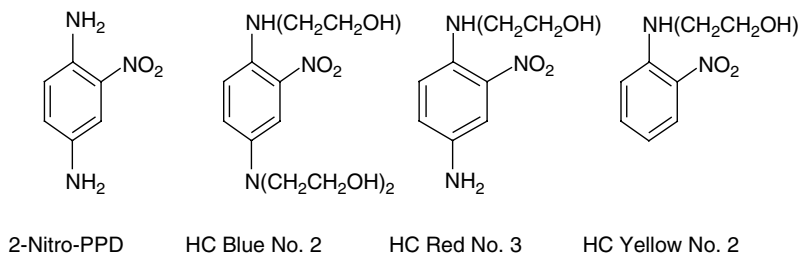
products' by which is meant 'not used with a separate developer product'. Only a few materials are allowed to be used in this way and these include dihydroxyindoline usually as the HBr salt and dihydroxyindole (the 5, 6 substituted isomer). These materials are not widely used as they were developed and patented by Henkel and L'Oreal respectively and are also not readily available, very expensive and sensitive to oxygen (this makes manufacture of products specialised). They have not found wide usage even in these companies and seem to have been restricted to limited usage in hair colouring products for men.

Products which use more conventional dye precursors such as PPD but rely upon aerial oxidation can be found but these are generally only sold in India and the Far East. It is generally believed in the EU that such products would not be safe for use and are not allowed by the EU Cosmetics Directive as they are described as 'oxidising colouring agents for hair dyeing' so this has to rely on the interpretation that aerial oxidation is not oxidisation.

Direct systems

The synthetic materials used in semi-permanent hair colouring systems were not introduced into cosmetics until the 1960s when the first products were created by Clairol. The first direct dye hair colouring formulators were hired by Clairol from the textile colouring industry and so some of these products still contain materials which originated from there. The most commonly used class of direct dyes is based upon aromatic amino compounds but usually contain an electron-donating nitro group which is located at ortho to the amino function. This gives a conjugated system which will be coloured and will (generally) also not take part in the oxidative colouring reaction with itself or with other PIs. Examples of this type of dye are given in Fig. 5.6. The simplest of these dyes is 2-nitro-p-phenylenediamine which is a good strong orange but has been recently banned for use in the EU although it is still allowed for use in the USA and some other areas. Further colours can be obtained by substitution of the amino functions and a blue/purple can be obtained by adding 3 hydroxyethyl groups to create HC Blue No. 2, a dye that is approved in the EU and still widely used. These dyes are generally quite water soluble but at higher concentrations surfactants and solvents may be needed to get them to dissolve in the desired product base. For a good discussion of how substitution affects the colour see Corbett (1998).

These dyes which do not contain a permanent positive charge rely on their ability to penetrate the hair shaft to give a colouring effect that lasts beyond one wash of the hair. They are therefore generally formulated into products with a relatively high pH at or around 10 which does cause the hair to swell. It is also important that the (effective) molecular size of the



Now banned in EU

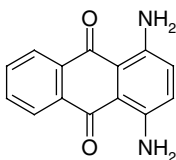
5.6 A selection of (soluble) direct dyes used in semi-permanent products.

molecule is relatively small to allow penetration into undamaged hair. It can be noticeable that the overall effectiveness of these dyes can decrease as the molecular size increases.

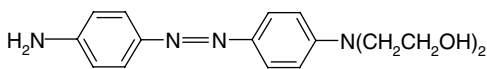
The second class of dyes that may be used in direct products is the disperse dyes and examples of these are given in Fig. 5.7. This type of dye has been widely used in the textile industry and the dye molecule has low water solubility. This can be a distinct advantage in direct colouring as the dye needs to be attached to a surface rather than in solution in order to encourage colour uptake. These dyes are generally dispersed using materials called lignin sulphonates and these may make up 50% by weight of the raw material; however, these added materials are not disclosed in the ingredients listing. Disperse dyes must be at least partially soluble in the product base otherwise they could not colour the hair. It is usually necessary to include solvents such as ethoxydiglycol or propylene glycol in the product base which can be used to solubilise/disperse the dyes into the formulation during manufacture. Disperse dyes generally have a larger molecular size and this means that they are generally not able to penetrate undamaged hair as easily as damaged, more porous hair. Therefore in semi-permanent products the disperse dyes are used to colour the damaged ends of the hair and are lost by washing less quickly than smaller dyes.

The number of disperse dyes available to the industry has dropped in the last 20 years and this is due mainly to doubtful toxicology (anthraquinones have a poor reputation in this respect) combined with the fact that these dyes are generally mixtures of a range of different compounds making characterisation difficult. A further practical difficulty is that the colours of these dyes may be standardised (particularly when produced for textile colouring) by the addition of other dye materials.

A third class of dyes used in direct systems are those which contain a permanent positive charge and are known as cationic or basic dyes (see Fig. 5.8 for some examples). These materials have a high affinity for the surface of

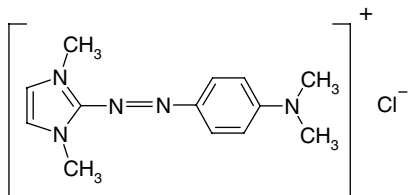


Disperse Violet 1

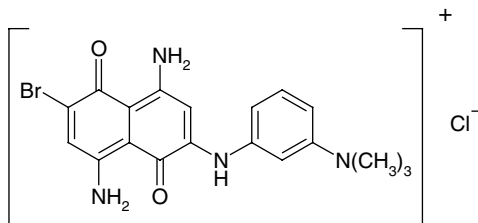


Disperse Black 9

5.7 Some disperse dyes used in semi-permanent products.



Basic Red 51



Basic Brown 16

5.8 Some basic dyes.

the hair, particularly that which is damaged and thus has a higher negative charge. Due to this affinity these dyes do not necessarily have to be used at higher pH and are often included in shampoo and conditioner systems at more conventional pH values. Due to the size of these materials and the high affinity for the hair surface these dyes are thought generally not to penetrate the hair shaft – an effect which is known as ‘ring dyeing’. Some of these dyes may contain azo functions and care should be taken to check that no breakage of the azo bond occurs if the pH value of the product is too high. One of the difficulties in using the basic dyes is that the colouring effect may vary with the degree of damage of the hair and the colour may be retained in the tips of damaged light-coloured hair for a long time but may not colour undamaged hair to the same extent. A further issue with these dyes is that they may contain non-coloured ‘extenders’ and these may be different in materials from different sources.

A fourth class of dye that can be used to colour the hair is the acid dyes which are more widely used as cosmetic colourants. These dyes are often described as temporary dyes and it is thus debatable whether they should be regarded as hair dyes at all under EU legislation. Their colouring ability from rinse-off systems at neutral or high pH is not very good due to their large molecular size and negative charge. However, it is possible to increase their colouring ability by using a lower pH system which decreases the negative charge present on both the dye and the hair. As the hair is not swollen at these lower pH values materials to swell the hair such as propylene carbonate may be added to these systems.

Direct dyes may also be added to oxidative systems to 'boost' the colour and this was done especially for red- and yellow-based shades. However as the oxidative dye precursors have improved somewhat in this respect this may no longer be necessary. The disadvantage of adding these colour boosters was that the colour washed out quite quickly thus the shades became dull quite quickly. In EU legislation, direct dyes may be supported for use in either oxidative and non-oxidative products or just the latter.

Other systems

A few types of material other than those described previously can be used to colour the hair. These come under the general heading of naturally derived materials and can be from plants or contain metal ions. In the early days of hair colouring many strange mixtures of materials were used to colour the hair and these were often made up in metallic containers with vinegar to lower the pH and to solubilise some of the metal. Only a very few of these are in use and many have been banned for toxicological reasons.

Lead salts were relatively recently banned in the EU for use in cosmetics due to their classification as a class 1 or 2A CMR. This classification in the Cosmetics Directive leads to an automatic ban in cosmetics regardless of any safety assessment. Products containing lead can still be bought in the USA as a 'progressive' hair colouring product used mainly by men. In the EU this metal was replaced by bismuth but this does not seem to work very well. Bismuth citrate has recently been placed on the list of the 123 supported dyes in the EU so someone must have produced a dossier. Oddly the only other metallic dye is silver nitrate which is approved for use as an eyelash and eyebrow colour.

Plant-derived dyes have a small place in the hair colouring market but their effects can be poor and variable when compared to the synthetic dyes. Only three materials are currently on the EU 'supported' list: henna, Lawsone (the active ingredient in henna) and indigo. *Curcuma longa* (Turmeric) was removed from the supported list in early 2010. A large number of other plant-derived materials are used in some other parts of the world but all these will become

unavailable in the EU when a positive list for hair dyes is created unless the large and expensive set of safety tests are undertaken in a timely fashion.

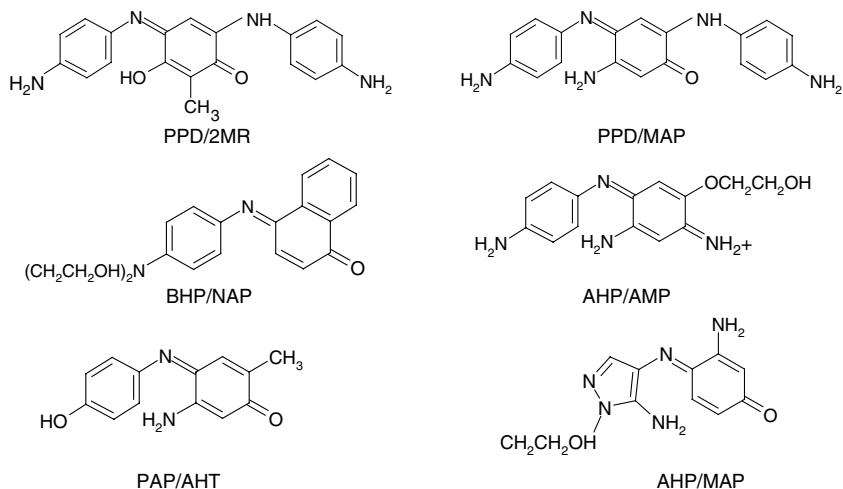
5.3.3 Oxidative hair colouring reaction products

Oxidative hair colouring products most often are supplied in two parts which are usually called the colourant and the developer. The colourant may be provided as a cream, a gel or a liquid and the developer most commonly as a thin liquid or a thicker emulsion (cream). The developer (or oxidising agent) may also be supplied as a powder (or a tablet) or could simply be aerial oxygen. The developer is most usually based on a hydrogen peroxide solution and as such has all the difficulties associated with this material. The developer is usually kept at about pH 3 (or lower) with stabilisers (e.g. chelating agents and free radical scavengers) and requires very careful control of metal ions which can cause (sometimes violent) decomposition or at least swollen containers.

The colourant is usually formulated at a pH above 10 although products with a lower pH have become popular recently. The dye precursors are in this formulation and are protected from oxidation during manufacture and storage before use by antioxidants, reducing agents and chelating agents. Upon mixing with the developer, just before use, the product will have a pH of somewhat less than the original colourant. In addition, the mixing of the product may cause a thickening and the formation of a suitable rheology (e.g. pseudo plastic) which allows the product to spread easily through the hair but does not drip onto the face and neck. This may be caused by the use of suitable surfactant mixtures or of (often acidic) polymers in one or both parts of the oxidative colourant product. This is an area which has been subject to much patent activity and should be approached with caution.

The rate of formation of the colour in the mixture must not be too fast as the final dye is intended to be formed within the hair and time must be allowed for the dye precursors to diffuse into the hair. This process is assisted by the high pH value which is known to cause the hair to swell. It is fortunate in this respect that hydrogen peroxide under these conditions is not a very good oxidising agent and it is believed that the colour formation reaction is catalysed by the hair itself. It is also possible that this catalysis is actually caused by the presence of metal ions within the hair for which the hair has a high affinity and which are also excreted into the hair from the body as the hair grows.

The nature of the final dye species within the hair has been the subject of some study and publication mainly by the Clairol Company. The best summary of this understanding is perhaps available as opinions from the SCCS/SCCP/SCCNFP and are available through the DG Health and



5.9 The structures of some oxidative dye 'couples'.

Consumer website (Health b–d). The original dossiers were requested by the Commission in order to satisfy questions concerning the possible skin penetration and toxicology of the reaction products of oxidative hair dyes. The structures of some of these 'couples' can be seen in Fig. 5.9.

5.4 Product types

Cosmetic products fall into a number of fairly straightforward technical categories. However, the advent of 'innovative' sales and marketing has led to a profusion of different descriptions for these products. Thus the products described here are in as generic a fashion as possible. Detailed descriptions of example formulations and methods of manufacture of decorative cosmetics can be found elsewhere (Riley, 2000; Schlossman, 2000). Many cosmetic products rely on forming emulsions of water, oil, wax and silicone in various proportions with one phase dispersed within another. The dispersion of a solid material adds to the complexity of these products and a good understanding of surfactant as well as surface and colloid chemistry is most useful in formulating cosmetic products.

5.4.1 Products with cosmetic colourants to colour the skin

These products are often called 'decorative' or 'colour' cosmetics or simply 'make-up'.

Eye shadow

Products to beautify the eyes have been used for thousands of years. An early product was known as kohl and this can still be bought today. 'Traditional' kohl should be regarded with great caution, however, as it traditionally contained heavy metals, particularly antimony, which is now quite correctly banned from use in cosmetics. Heavy metals were extensively used and were very useful in cosmetics (particularly lead) and recent work (Tapsoba, 2009) has shown that a great deal of scientific understanding may have gone into the production of Egyptian cosmetics which also may have had (deliberate) therapeutic properties. Eye shadows may come in the form of powders or creams (really thickened oil systems) and need to be carefully formulated to give the correct in-use properties. The products must spread easily without unnecessary catching on the sensitive eye area. Preservation or the prevention of the growth of micro-organisms is very important (and can be difficult) in these products as this type of contamination can cause blindness.

Mascara

Mascara is essentially pigment dispersion in a product that will form a film on the eyelashes. Material can be added such as nylon which gives the impression of added length and volume. Early mascara came in the form of a cake and now there are also creams with waterproof properties.

Eyeliners

Eyeliners may come as liquids to be applied with thin brushes or a pen-like applicator or can be in the form of pencils. The product must apply easily so as not to pull the sensitive area but must also be smudge- and waterproof. The creation of pencils is an art in itself and requires specialist equipment as well as knowledge.

Lipstick/glosses/liners

Lipstick/glosses/liners are products to be applied to the lips can be the most striking and noticeable of all decorative cosmetics and must be made from materials that are safe to eat as well as have an acceptable taste. The challenges for lipsticks in particular are high and the manufacture as well as the packaging of the product can be particularly difficult. Lipsticks are essentially suspensions of pigments in a wax and oil medium which must have suitable spread and long-lasting characteristics but without smudging and transfer to other surfaces. The selection and concentrations of the waxes and oils is critical. In addition lipsticks may now have other functions such as sunscreen activity.

Lip glosses are thinner products and may be applied with the finger or some type of applicator including roller balls. Lip liners usually come in the form of pencils with similar issues to eyeliners.

Foundation make-up

An older version of this product type was known as cake foundation which was used in theatrical make-up but this has largely been replaced with liquid foundations which are emulsion products with water in silicone being the most modern systems. These modern products give the best in-use characteristics but they can be expensive and difficult to render the pigments stable, i.e. not flocculate and move to the surface. Modern products tend to offer additional functions in addition to a good base colour such as UV protection and the delivery of vitamins and other skin care 'actives'.

Face powders

Face powders can either be in the form of loose or compressed powder. A common major component of these products is talc (hydrated magnesium silicate) and this needs to be free from asbestos as well as from micro-organisms which have been an issue with this (naturally occurring) material. A wide variety of other solid materials as well as binders in the compressed powders may be found in these products.

Nail varnish

Nail varnishes or lacquers are usually sold in small bottles with an applicator brush and may come in two parts, i.e. a base coat and a top coat. These products are essentially a suspension of pigment in an organic solvent which also contains a film-forming polymer, a resin and perhaps a plasticiser. As these are non-aqueous systems it may be difficult to prevent settling of the pigment. This can be prevented by the use of a material such as organically modified clay which can achieve high low shear viscosity in these systems with a degree of thixotropy. This may be achieved by forming a system that is loosely flocculated and which breaks up on shearing and reforms on standing. These systems give stability to separation and caking but retain a low 'application' viscosity.

5.4.2 Products often with cosmetic colourants to colour the product

Shampoos, body wash, shower gel, hand wash, liquid soaps

These products can be very similar in chemical composition and are most likely to contain water-soluble dyes but care usually has to be taken to

protect the dye from the effects of solar radiation. This is usually best achieved by packaging in an opaque container and making sure that metal ion contamination either from water or other raw materials is kept to an acceptable minimum. If a transparent container is used chelating agents are usually added and UV absorbers may be introduced to either the formulation or the packaging. Even with these precautions fading or colour changes can often take place but can be slowed to an 'acceptable' level. These products are most likely to be based on anionic surfactants and shampoos may contain conditioning ingredients such as silicones and cationic polymers.

Hair conditioners, rinses, masques, treatments

These products have very similar issues to shampoos etc. mentioned above, but they are generally based on cationic surfactants in combination with fatty alcohols as well as added silicone materials. Care may need to be taken to avoid interaction between acidic (anionic) colourants and the cationic surfactants.

Self-tanning products

Self-tanning products are often a lotion or a spray that contain a material, e.g. dihydroxyacetone (DHA), which reacts with the skin (through a Maillard reaction) to form a brown (or sometimes somewhat orange) colouration in the upper layers of the skin which grows and washes out in perhaps 2 weeks. This material is not regarded and regulated as a cosmetic colourant in the EU. However, the products often contain water-soluble colourants to colour the skin initially to show where the product has been applied and before the colour is formed on the skin. It can be quite a challenge to get the colourants in this product type to stay stable and off-colours such as green can be formed.

Solid soap

Soap is a very complex soft-to-hard solid made up of fatty acids and other materials. It is often sold in its natural white form (if the starting materials are sufficiently pure) but a yellow coloration may develop with oxidation and antioxidants may be added. Colourants may be added to the soap at sufficiently low levels not to colour the skin. These can be added in swirling patterns via extrusion processes.

Toothpaste/mouth wash

The usual colourant in toothpaste is titanium dioxide and it is usually white. Other colourants can be added, often blue or red, sometimes in the form of stripes either by co-extrusion or with clever packaging design.

5.4.3 Products intended to colour the hair

Hair dyes are used in products designed to colour the hair either in an extreme or a very subtle fashion. The primary function of hair colouring products used to be to cover grey. However, more recently it has become fashionable to change the colour of the hair radically and achieve multi-colouring effects which can be striking in the extreme.

Level 3 or permanent colourants

Permanent colourants contain two parts which are sold together in cartons to the retail market or separately to the salon trade and the colour is expected to last until the hair grows out in about 4–6 weeks. Permanent colours usually contain ammonia in the colourant which enables the product to lighten the underlying hair colour (natural or artificial) and these are the most effective and versatile of all current hair colouring products. Permanent colours have also been produced containing monoethanolamine (MEA) and these have been marketed as having a nice fragrance but usually cannot give the lightening levels associated with ammonia. It is very difficult to mask the odour and impact of ammonia with a fragrance. These products are the best ones available to cover grey effectively and to give a wide range of colour effects. A recent innovative product launch claims to be able to lighten the hair to the same extent as ammonia but with the use of MEA.

Level 2 or demi-permanent or tone-on-tone or long-lasting semi-permanent colourants

Demi-permanent colourants are also oxidative colourants but do not contain ammonia and are not intended to lighten the hair at all. Often these products are claimed to last 'up to' 28 washes although it is still possible to achieve a 'permanent effect' with 'no ammonia' products. Sometimes the problem with these is that the colour does not actually wash out as fast as claimed. To avoid consumer complaints these products should only be used on hair colour that is close to the intended shade. It is generally easier to achieve this demi-permanent effect with fashion colours as the dyes used to effectively cover grey tend to form larger more insoluble dyes in the hair and thus are hard to remove with washing.

Level 1 or semi-permanent colourants

Semi-permanent colourants have received much less commercial support in the last 20 years than have the oxidative colourants and this has resulted in less of this product type being sold. It is now quite difficult to purchase a 'grey coverage' semi-permanent or one designed to be used as a 'toner' on pre-lightened hair. This type of product is still more widely available in 'fashion' colours. It

can be quite difficult to obtain a consistent tonality across the hair with direct dyes due to the differing condition on the hair from root to tip. This problem may be seen particularly during the wash out of this product type.

Colour 'reviving' or 'boosting' shampoos and conditioners

This type of 'maintenance' product has become more fashionable in recent years and is usually based on anionic or cationic dyes depending upon the degree of colour deposit that is required.

Shampoos for grey and bleached hair

Grey and bleached hair can sometimes acquire an unpleasant yellow tonality and this can be countered by the addition of a blue or purple coloured dye which moves the yellow colour to a more neutral or ash shade. This type of product used to be widely known as a 'blue rinse' and they still have a place in the market.

5.5 Future trends

The future trends in the colourants and dyes area are mainly affected by the legislation in the cosmetics area and changes which occur. The main reason for the loss of materials to EU regulation is due to the unwillingness of the industry to 'defend' the materials, i.e. prepare the required safety information as defined by the SCCS. This is usually due to economic factors rather than poor toxicology. Due to the high cost of the creation of safety data it is also true that the only companies able to undertake this are the large multinationals. New materials emerging from this source will tend to have patent protection thus preventing general usage for a number of years. In some cases companies do group together to spread the cost but this tends to occur only for 'important' and widely used old materials. As there are many patents which suggest new ways of colouring the hair and of producing colour these cannot be covered here but a few examples will be given.

A good example of a rare new hair dye molecule appearing on the market in a product is 2, 3-Diaminodihydropyrazolo Pyrazolone Dimethosulfonate. This hair dye has appeared on the US market and has made it on to the EU list of 123 supported dyes. This means that a safety dossier must have been produced relatively recently. This hair dye has been developed by L'Oreal and is of course patented (see for instance Vidal, 2007). The material is a PI and is claimed to be an improvement upon the known diaminopyrazoles giving good red and copper shades. It is also claimed to be more resistant to external influences such as sunlight and washing as well as being able to produce colour at more neutral pH values than usual. This new hair dye material may not become

generally available for a number of years but still only represents more of the same chemistry that is currently used in oxidative hair dye products.

In addition the ability to undertake safety testing on cosmetic raw materials is becoming limited as a series of prohibitions on testing chemicals on animals intended for cosmetic use are coming into force with a total ban (relating to materials used in products to be marketed in the EU) eventually to follow. As the creation and validation of alternative (non-animal) tests is lagging behind this ban it is likely that the introduction of new materials into the EU market for cosmetic usage may cease entirely. This situation is somewhat perverse as this legislation will prevent the introduction of novel materials which might not have the drawbacks exhibited by some of the materials used currently especially as oxidative hair dye precursors. In addition to the cosmetics regulations there is also the impact of the EU REACH (Registration, Evaluation, Authorisation and restriction of Chemicals) regulation on chemicals in general where the testing of chemicals (perhaps on animals) is demanded by the legislation.

Hair dyes derived from plants have been used to colour the hair and body for many thousands of years. The combination of these materials with metal ions, often to act as mordants, is also a very old practice. Recently a 'new' technology has been placed on the market in the USA by a company called Advanced Cosmetic Technologies. This is in response to modern consumers' desire to use 'safe' and 'sustainable' products. The technology behind this two-part product (plant extracts in one part and metal ions in the other) is described in patent applications (see for instance Greaves and Greaves, 2009). This product is generally only available through the internet and it remains to be seen if it has any significant impact on the hair colouring market. Interestingly this product is probably legal for sale in the EU at present, but if a positive list is enacted all the naturally derived hair dyes will need (in principle) to pass through the defined safety dossier process.

Regardless of all this regulatory activity the patenting of a vast range of materials especially for use as hair dyes continues and it is an interesting question why so little of this patent activity actually appears to be used in finished products. It is possible that none of the replacement systems is as good (or as cost effective) as current products. It is also true that existing (multinational) companies have a large investment in current product formulations and do not wish to alter these until it is necessary either from a commercial or a regulatory point of view.

The outlook for innovation in this area is therefore somewhat bleak (especially in the EU) as the introduction of novel materials is made increasingly difficult. A situation in the future can be foreseen when a new generation of products could be introduced in the USA and areas that do not follow the EU which are better and superior to EU products but they will not be allowed for sale within the EU.

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M. WAINWRIGHT, Liverpool John Moores University, UK

Abstract: Due to the use of dyes as biological stains, dye therapy was the initial basis for chemotherapy and many modern drugs have dye antecedents. Dyes used in the medical field today may certainly be found as drug colourants, in vital staining, tracing and histopathology, but some also remain as chemotherapeutics. More modern applications include photosensitisers in light-activated therapies for cancer and infection and biocidal dyes for use in medical textiles. Such areas have also contributed to an increasing knowledge base concerning dye toxicity and mutagenicity.

Key words: biological stains, dye therapy, photodynamic antimicrobial chemotherapy, photodynamic therapy, dye toxicity.

6.1 Introduction

6.1.1 What is the 'medical industry'?

Good health is the cornerstone of modern life. Normally when we are ill, our main aim is to return to a state of good health yet, having done so, we tend to take it for granted. Prevention may be better than cure, but considerably more funding is dedicated to the latter than to the former! Those of us fortunate enough to live in rich nations have ready access to healthcare 'from the cradle to the grave' – indeed, constant advances in technology have made healthcare provision an all-pervasive aspect of twenty-first-century life in developed nations. The product range of the modern medical industry includes both the tangible – drugs, machinery, beds, etc., and the intangible – support services, counselling, etc.

It may not be obvious that dyes have a significant part to play here. However, much of the modern pharmaceutical industry is, in fact, based on dyes and their interaction with tissue, following discoveries made in the late nineteenth century by scientists such as Koch, Ehrlich and Gram (Wainwright, 2003b).

6.1.2 Dyes and medicine

Consider, for example, a hospital patient with a sore throat. If the cause is thought to be bacterial, the supervising clinician will order a swab test – i.e.

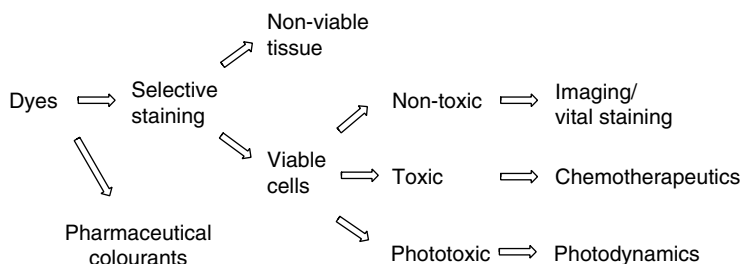
the analysis of cells taken from the back of the throat. Part of this analysis will consist of microscopic examination of the cells stained with a combination of dyes – usually the triphenylmethane crystal violet and iodine, followed by an alcohol rinse and then the phenazine derivative, safranin. If bacterial cells are present, they usually appear either purple or reddish brown, depending on whether or not the crystal violet is retained after the alcohol rinse. This is, of course, the Gram staining procedure: Gram-positive bacteria, e.g. streptococci, retain crystal violet, Gram-negatives, e.g. *Haemophilus influenzae*, do not.

Having identified a bacterial infection, the clinician will probably order a course of antibiotics for the patient. In paediatrics, for example, a suspension of the penicillin derivative amoxicillin is quite usual. To make this more palatable and acceptable, various additives are often included in the suspension, including a flavouring and a dye, quinoline yellow. Amoxycillin capsules often have two coloured halves from red and yellow azoic dyes.

Thus, even in this relatively simple presentation, several dyes have been identified.

Plainly, there are likely to be other colourant uses in the patient's environment, such as the textile dyes used on bed linen, pigments in the paint on the walls of the ward, etc., but these dyes and pigments are not *specifically* used in healthcare. The examples covered in this chapter are intended to have particular relevance to the medical industry and, for the most part, this has been taken to mean that they interact in some way with patients. An outline of the rationale for the use of dyes in healthcare is given in Fig. 6.1.

From Fig. 6.1, it may be appreciated that there are three main areas for dye usage within healthcare – colouration of pharmaceuticals, staining of cells and chemotherapy. The first two were developed over a similar time period, as noted above, whereas the third grew out of cell staining and actually supplied the first chemotherapeutic agents before withering under the



6.1 Rationale for dye use in healthcare.

glare of penicillin and subsequent antibiotics. Yet this third area has been revitalised in recent years due to burgeoning interest in the possibilities offered by the photodynamic approach, ironically in the face of widespread bacterial penicillin resistance.

6.2 Dyes for indication

6.2.1 Biological stains

Colouring biological samples is similar, in scientific principle, to textile dyeing. In both areas, dyes are added to a material with the object of dye molecule attachment, usually to a polymeric substrate. However, where in textiles the chemical make-up of the substrate is well established – cotton/cellulose, silk/protein, etc. – allowing considerable control of the resulting colour and shade, biological samples are usually a complex chemical mixture, the resulting colour and colour distribution depending on the relative proportions of different biopolymers. The proportion and distribution of these biopolymers will also vary depending on the growth phase and age of the cell.

As mentioned above, the Gram staining procedure provides the cornerstone of rapid identification of bacteria in our hospitals. The process was developed by the Dane, Christian Gram in 1884 – pioneering work in an era which was less than accepting of the ‘Germ Theory’ of disease. Such research, built upon by contemporary scientists such as Robert Koch, Paul Ehrlich and others (Leishmann, Romanovsky, Giemsa – the list is fairly substantial) eventually developed into the scientific branch of histology (Wainwright, 2003b). Specialisms within histology include histopathology, i.e. the study of disease processes via staining, which is really what Gram and subsequent workers set out to do. Modern medical laboratory scientific officers carry out such bacterial staining routinely, alongside further biochemical testing to give information on specific strains of bacteria, particularly in terms of drug susceptibility.

Biological stains thus remain of immense importance in modern medicine from the point of view of infection control. However, cell staining is much more extensive than just the differentiation of bacterial and human cells.

Usually, medical microbiologists examine cell samples taken from patients. These samples normally include blood, sputum, urine, faeces or tissue swabs, depending on the disease presentation. The process then runs along the lines of ‘Is there an infective organism here? If so, what is it?’ Other disease states may not be so easy to pinpoint – for example where the problem lies in human cell differentiation. Obviously, if such differentiation is required within the live patient, there are more stringent requirements in terms of dye toxicity (*q.v.*) than would apply to the examination of extracted tissue samples.

Although it is a gross oversimplification, *Homo sapiens* may be considered as a highly complex collection of cells, ideally working together. Where there is aberrant cell behaviour – e.g. incorrect biochemical function or unrestricted growth, organic disease normally results – for example, diabetes and cancer, respectively.

Diabetes arises from the lack of production of the hormone, insulin, by cells of the pancreas known as the Islets of Langerhans. Such a lack of chemical production would be difficult to demonstrate simply and rapidly under a microscope with a staining technique. It is much simpler to test the blood or urine for the glucose level, since this is in turn governed by insulin. This can also be demonstrated using dyes, but is not a staining technique (see below).

Cancer normally presents as a rapid, unrestricted cell growth, either in parts of the body where such cells should not occur (e.g. brain tumours may be secondary melanomas) or outside the limits of normal growth – for example where a tumour blocks the oesophagus. Such abnormalities may be seen in a tissue biopsy under the microscope with suitable staining – often haematoxylin-eosin – but often it is better to stain the suspected tumour site itself, in order for remedial action to be taken directly – e.g. surgical debulking or laser ablation. This is particularly true of pre-cancerous conditions such as Barrett's oesophagus, for which dyes such as methylene blue may be used to delineate the aberrant tissue, prior to surgery or laser treatment (see also photodynamic therapy (PDT), below).

Dye affinity may also be used to this end, for example in the difficult tracing of melanoma microsatellites (metastases) in the bloodstream. The high affinity of phenothiazinium dyes, such as methylene blue, for the biopolymer melanin led to the use of radio labelled dye – either with radioactive sulphur in the ring, or with an iodine-125 substituent – as an efficient tracer (Link *et al.*, 1989).

Similarly, cancer-screening programmes are invaluable in saving lives. A good example of this is screening for cervical cancer, which still uses the 'Pap' (Papanicolaou) stain to differentiate normal and aberrant cells in cervical smears (Nanda *et al.*, 2000). More recently, the use of 5-aminolaevulinic acid, a cellular precursor of protoporphyrin IX, has been employed for the indication of rapidly metabolising tumour cells *in situ*, relying on the increased fluorescence associated with greater levels of PPIX produced by such cells (Jocham *et al.*, 2008).

A simpler, more user-friendly, example here concerns the use in oral hygiene of disclosing tablets. These tablets usually contain erythrosine, a xanthene dye, which stains the polysaccharides present in bacterial biofilms built up around the gum/tooth margin (Marsh *et al.*, 1989). Periodical use of such tablets can thus give the user an ongoing picture of the potential for gum disease. Since disclosure tablets are available over the counter, this approach allows considerable patient control over oral hygiene.

6.2.2 Tracer dyes

Thus far, the biological stains mentioned have been used to demonstrate tissues, i.e. in differentiation. A second classification includes stains used for fluid pathway delineation, typically in the bloodstream or lymphatics.

Both methylene blue (phenothiazinium) and patent blue (triphenylmethane) are used in *in vivo* tumour tracing and staging (Rzyman *et al.*, 2006). Methylene blue has been shown to be a safe, effective option for the tracing and localisation in sentinel lymph node biopsy, for example in the monitoring of potential axillary spread in breast cancer, indeed to be as effective as radiotracing techniques (Varghese *et al.*, 2007). This is particularly useful given that hospital access to nuclear medicine is not universal.

Similar dye-tracing approaches are in use for a range of neoplastic disease, including gynaecological, colorectal, thyroid and lung (Cox *et al.*, 2002; Rzyman *et al.*, 2006; Tsugawa *et al.*, 2002; Yuan *et al.*, 2007).

The conjugation of dye molecules with tumour-targeting peptides or other biomolecules also allows selective imaging, the ultimate aim being to use such indicators intraoperatively. To this end, several rhodamine derivatives have been synthesised as probes for the somatostatin receptor, which is over-expressed by several tumour types (Mier *et al.*, 2002). Similarly, up-regulated levels of polyamine transporters in tumours have been targeted using fluorescent spermidine-acridine conjugates (Wolf *et al.*, 2006). The availability of tumour-specific monoclonal antibodies also allows fluorescent labelling, for example using cyanine dyes (Xu *et al.*, 2009).

Both the cyanine, indocyanine green (ICG) and the xanthene dye sodium fluorescein are used in the measurement of blood circulation *in vivo*, on the basis of near-infrared absorption and high fluorescence respectively allowing visualisation through body fluids (Dzurinko *et al.*, 2004). Both macro- and microvasculature may be investigated using indocyanine green, for example during coronary bypass procedures (Desai *et al.*, 2006), and in the examination of choroidal neovascularisation in age-related macular degeneration (Slakter *et al.*, 2000), respectively. ICG is also employed in fluorescence tracing of sentinel lymph nodes in cancer patients (Fujiwara *et al.*, 2009).

6.3 Dyes as colourants in medicines

As mentioned in the introductory section, medicines may be purposely coloured in order to increase their acceptability – for example, the amoxicillin paediatric suspension cited is (supposedly) made more palatable to children by the combination of banana flavouring and yellow colouring. The use of contrasting, coloured halves in plastic capsules may be useful in rapid drug identification, although this is plainly not a failsafe approach. The inclusion of colouring agents (Table 6.1) in tablet coatings for aesthetic

Table 6.1 Dyes licensed for use as colourants for pharmaceutical preparations

Colour	Azoic	Indigoid	Quinoline	Triaryl/methane	Xanthene	Natural	Inorganic
White							
Red	Allura red Amaranth Azorubine Ponceau 4R Sunset yellow				Erythrosine Phloxine B	Cochineal	Titania Iron oxide
Orange						β -Carotene Canthaxanthin	
Yellow	Tartrazine		Quinoline yellow				Iron oxide
Green							
Blue		Indigo carmine		Brilliant blue Patent blue V	Chlorophyll		
Black							Iron oxide

Source: Adapted from Jones (2004).

reasons is less easily understandable, particularly where they may be mistaken for sweets by children.

Dyes used in medicines are now few in number, mainly on the grounds of potential associated toxicity. Indeed, the small group given in Table 6.1 is only likely to decrease in size and for the same reason. Long-term therapy with the same coloured therapeutic agent offers the potential for toxicity, thus it is important to understand how ingested dyes are metabolised – in the same way that conventional drug toxicity is studied. Such investigation is discussed in Section 6.6.1.

Table 6.1 features a full range of colour, plus black and white, from a group of twelve synthetic and four natural dyes, alongside the inorganic pigments titania and various forms of iron oxide. Among the synthetic dyes, half are of the azoic class.

6.4 Dyes for therapy

6.4.1 Conventional chemotherapy

The conventional view of coloured therapeutics, certainly in Western medicine, is that they should be avoided wherever possible. The basis for such opinion, which seems to cut across both the medical and pharmaceutical fraternities, is usually twofold: that patients would react badly to skin or other body colouration resulting from therapy, and that dyes are toxic, aren't they?

The first criterion may be true, or not. It is impossible to say that all coloured medications result in colouration of the patient. The administration of *any* substance to a human may lead to the metabolic alteration, or destruction, of that substance. It may also lead to the patient appearing to be a different colour post-administration, if only temporarily. However, if the required benefit is attained in terms of patient health there is a balance to be made. Plainly this does not apply if there is an equivalent, non-coloured therapeutic. Notably, in a recent trial of methylene blue for the treatment of falciparum malaria in children in Burkina Faso, the subjects' urine and nappies were coloured blue as a consequence, but education of those involved allowed widespread acceptance and compliance (Meissner *et al.*, 2005).

The toxicity of dyes is also subject to sweeping generalisations, but is governed by a similar argument. There are many different structural types available, with a variety of physicochemical properties, so toxic effects in a human patient depend on the usual administration/distribution/metabolism/elimination (ADME) profile pertaining to conventional drugs (see Section 6.6.2). However, it is true to say that certain dyes – those derived from benzidine, for example – are known to have adverse effects in humans (Degen *et al.*, 2004), and that often dyestuffs are derived from toxic chemicals and contain

these as impurities. Clearly action would be necessary on both counts to ensure that patients were not exposed, both by ‘designing out’ structural features like benzidine and ensuring product purity.

The relationship between modern pharmaceutical drugs and dyes is close. Many therapeutic agents in the twenty-first-century clinic were originally derived from dyes produced a hundred or more years ago. For example, methylene blue, originally reported to cure malaria in 1891, was subsequently used as a lead compound for anti-malarial drug discovery in the 1920s and 1930s, both in Germany and the USSR (Wainwright and Amaral, 2005). The acridine and quinoline anti-malarials, such as mepacrine and chloroquine respectively, were produced as a direct consequence of this. Similarly, the basic side chain originally used to produce anti-malarial methylene blue derivatives, and featured in both mepacrine and chloroquine, may also be seen in drugs used for the treatment of depression and schizophrenia (Wainwright and Amaral, 2005). Others of Ehrlich’s discoveries also provided chemotherapeutic agents in various forms: during World War One, aminoacridines such as proflavine and acriflavine, were the first widely used synthetic wound antibacterials (Browning *et al.*, 1917); the dyes trypan red and trypan blue, effective against trypanosomiasis (sleeping sickness) in mice but not in man, led to the development of the non-staining drug suramin; series of azoic dyes screened by Gerhard Domagk at Bayer in the 1920s and 1930s led to the discovery of the antibacterial action, *in vivo*, of Prontosil, later discovered to be a pro-drug form of sulphanilamide. Thus were the sulphonamide antibacterials developed.

Given that chemotherapy evolved from dye therapy, thanks to Ehrlich and his peers, it is not surprising that there were many coloured therapeutics in the clinic in the first half of the last century. Most of these disappeared with the access of the medical profession to drugs which were firstly more effective and secondly non-colouring. Even given this logical evolution, however, a range of dyes remains in clinical use today, although not always in the original, intended application.

Crystal/gentian violet

One of the key events during the very early development of the new aniline dyes as biological stains was the introduction of the Gram stain (see Section 6.1.2). The use of gentian violet (crystal violet) as a bacterial stain led, eventually, to its use as an antibacterial. Both gentian violet and the related dye brilliant green were employed against wound sepsis alongside proflavine and acriflavine during World War One, as covered above. Gentian violet was also found to be active against fungi, and was used until relatively recently against skin infections such as ringworm (Laube, 2004). In a parallel field, the dye is added to donated blood by South American agencies to inactivate the parasite

responsible for Chagas' disease, *Trypanosoma cruzi* (Esteve *et al.*, 2002). Finally – and very encouragingly for those involved in anti-infectives research – crystal violet proved to be effective in the treatment of patients infected with methicillin-resistant *Staphylococcus aureus* (MRSA) (Saji *et al.*, 1995).

Methylene blue

Again due to Ehrlich's efforts in the late nineteenth century, methylene blue was widely tested as a potential therapeutic against many forms of infectious disease. Although its activity against both bacteria and fungi is weak, its human toxicity is also very low, allowing its use in vital staining and surgical indication, as mentioned previously. Guttman and Ehrlich's cure of two malarious individuals in 1890 has proved a recurring lodestone in anti-malarial research (Wainwright and Amaral, 2005), and underpins its recent clinical trialling in Burkina Faso. Due to a combination of its low toxicity and useful redox potential, methylene blue is also a first line treatment for cyanide poisoning and methaemoglobinemia (Laverge *et al.*, 2006). See also Section 6.5.

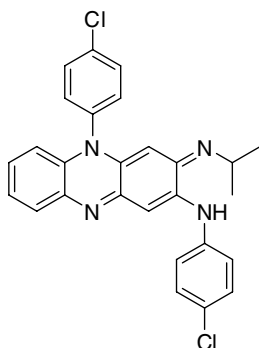
Acridines

Although in the vanguard of therapeutic dyes before the dawn of the 'antibiotic era', drugs such as proflavine and acriflavine became back numbers with the ready availability of effective agents such as the penicillins, tetracyclines, etc. However, proflavine retains a minor role in local antisepsis, typically in burns units, while acriflavine has been used in AIDS patients as an inhibitor of viral replication (Mathé *et al.*, 1997). The related compound ethacridine (Rivanol) also finds occasional use in cases of shigellosis (dysentery) (Wainwright, 2001). Elsewhere, the DNA-binding capability endowed by the acridine chromophore has provided the basis for several current anti-cancer agents (Finlay *et al.*, 1996).

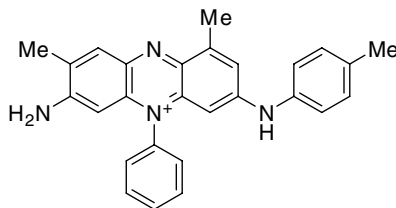
Phenazines

Replacement of the C-9 carbon in the acridine with nitrogen generates the phenazine nucleus, responsible for biological stains such as neutral red and safranin, among others. Although a range of phenazines was examined for antimicrobial activity in the post-World War One period (Browning *et al.*, 1922), none appears to have been very effective. However, a phenazine-containing molecule has formed part of the antibacterial armoury since the 1950s. Clofazimine (Fig. 6.2) was originally synthesised by Barry in the search for anti-leprosy drugs (Barry *et al.*, 1948).

Containing the phenazine chromophore as a quinoneimine, clofazimine is a purple/damson coloured compound. Although it was originally aimed



Clofazimine



Mauveine

6.2 Clofazimine (quinoneimine) and mauveine.

at Hansen's bacillus (*Mycobacterium leprae*) (Lockwood, 2005), it exhibited activity against *Mycobacterium avium*, one of the opportunistic pathogens associated with HIV-positive status (Arbiser and Moschella, 1995). Clofazimine has also found use in the treatment of Crohn's disease (Selby *et al.*, 2007), and in drug-resistant tuberculosis (Shah *et al.*, 1993).

It is interesting to compare the structures of clofazimine and Perkin's mauve (Fig. 6.2), particularly given the fact that Perkin was actually trying to synthesise another therapeutic molecule, *viz.* the quinoline anti-malarial quinine.

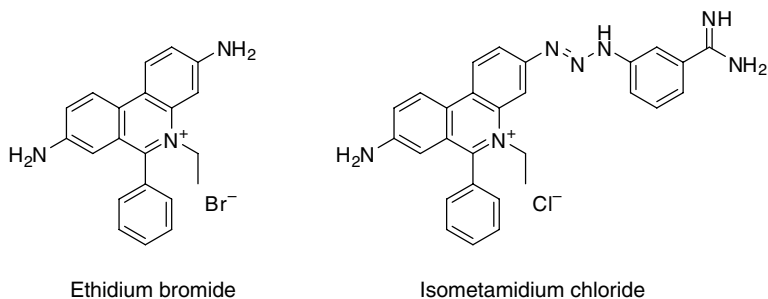
Phenanthridines

Given the amount of research carried out on acridine-based drugs, it is not surprising that the isomeric phenanthridine ring system has also produced several notable compounds. Suitably substituted phenanthridines exhibit similar properties to the acridines covered above. For example amino derivatives where the amino groups are conjugated with the ring nitrogen (e.g. ethidium bromide) are usually highly cationic in nature and exhibit high nucleic acid affinities.

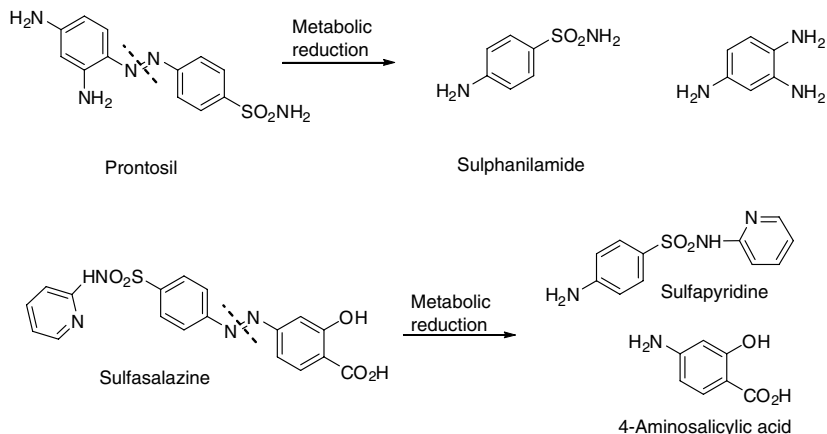
Phenanthridines were developed for intentional use in tropical medicine – for example in human African trypanosomiasis (sleeping sickness) after World War One (Browning *et al.*, 1938). Ethidium bromide and later derivatives such as isometamidium chloride (Fig. 6.3) are established trypanocidal agents (although mostly now used in the veterinary milieu), and are known to target the DNA of the trypanosomal (Boibessot *et al.*, 2002).

Azoic compounds

The discovery that it was the known sulphanilamide and not the Bayer dye Prontosil that was an active antibacterial agent led to a synthetic feeding frenzy in the 1940s among chemical and pharmaceutical houses as a



6.3 Phenanthridine-based trypanocidal agents.



6.4 Drugs based on the reduction of azoic dyes.

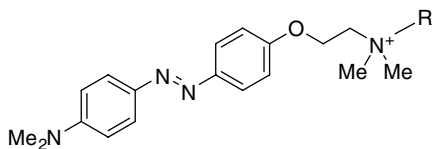
plethora of 'me too' compounds of the sulphonamide class that were produced. Since Prontosil and its analogues are ineffective without metabolic activation – i.e. the release of the sulphonamide moiety following reduction in the gut of the azo linkage (Fig. 6.4) – it is logical that the thousands of drug candidates produced subsequently were sulphanilamide derivatives, not azoic dyes. However, the *in vivo* azo reduction step has been employed to clinical advantage, since it was recognised that this could be used as a bowel delivery system. Thus the drug sulfasalazine is broken down in the colon to its constituent parts, sulfapyridine and 4-aminosalicylic acid (Fig. 6.4), both of which are anti-inflammatory, as a treatment for ulcerative colitis (Dichi *et al.*, 2000).

6.4.2 Antimicrobial dyes for medical textiles

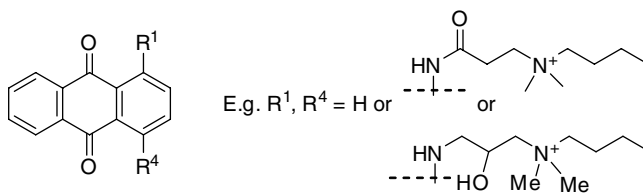
One of the major problems for fabric longevity, particularly during storage periods, is fungal growth. Plainly this may be addressed by the use of

biocidal agents, but the examples given in the preceding description support the application of textile dyes which are also biocidal in nature. Thus, both colouration and antimicrobial action would be effected by the dyeing process.

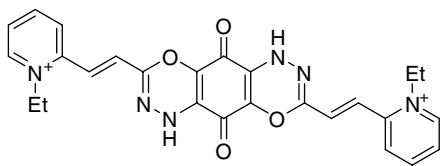
This is obviously an efficient approach to fabric protection, but it could also be extended to protecting patients in the continuing fight against healthcare-acquired infections, since many infections are communicated via the environment – soft furnishings, bedding, hospital scrubs, etc. Several biocidal agents are employed in disinfectants for healthcare, being active against MRSA and other important hospital pathogens. Dyes having similar structural motifs have been produced, for example, quaternary ammonium salt derivatives (Fig. 6.5). Since the majority of textile dyes contain amino functionality, the synthesis of these biocidal analogues is relatively straightforward, as reported both for simple azoic (Liu *et al.*, 2007) and anthraquinone derivatives (Liu and Sun, 2009) (Fig. 6.5). Antibacterial cyanine dyes of overall cationic nature have also been reported (Fig. 6.5) although, since the positive charge in such cases is delocalised throughout the chromophore,



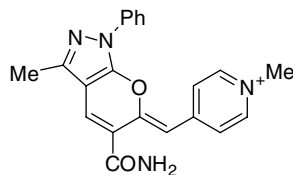
Azoics, R = *n*-propyl, *n*-octyl, *n*-dodecyl



Anthraquinones



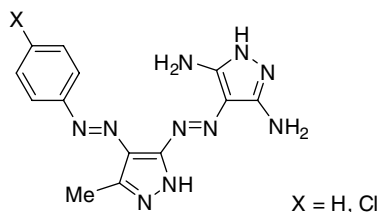
Oxadiazine derivative



Pyrazole derivative

Cyanine-type

6.5 Antimicrobial textile dyes.



6.6 Antibacterial/antifungal bis(azoic) dyes.

molecular interactions with bacteria may be different from those of the point charges presented by the quaternary ammonium salt azoics and anthraquinones mentioned, these most probably interfering with bacterial membrane dynamics.

Interestingly, a series of bisazo dyes, based on the pyrazole nucleus (Fig. 6.6), proved to be highly active against both bacteria and fungi, in some cases being more effective than the standard chemotherapeutic agent fluconazole (Karcı *et al.*, 2009). Thus, as well as providing potential agents for textiles, novel leads have been produced for conventional drug discovery/development.

As covered previously, there are still several dyes in use as therapeutics. However, the use of the antimicrobial examples in medical materials appears very scarce. Only brilliant green has been reported in such application, in conjunction with the standard biocide chlorhexidine as an antimicrobial treatment for latex and nitrile examination gloves (Reitzel *et al.*, 2009).

In considering the use of antimicrobial textile dyes, it should be appreciated that conventional biocidal agents (chlorhexidine digluconate, benzalkonium chloride, etc.) are usually employed at relatively high concentrations – for example, in comparison to conventional antibacterial drugs. Such levels may prove difficult to attain in practice on the surface of a textile. Another consideration, undoubtedly, would be the colour imparted to the substrate. For example, the antifungal bis(azoic) dye shown in Fig. 6.6 is bright orange. Would this colour be acceptable for operating theatre scrubs?

6.5 Medical photosensitisers

As the term suggests, *photosensitisation* is a process by which a substance is activated or changed by the application of light energy. Substances which mediate this process are, thus, *photosensitisers*. While the current chapter is concerned with their medical application, photosensitisers are encountered elsewhere, for example in plant photosynthesis or in industrial oxidation processes. Skin reactions to chemicals, especially drugs, are often manifestations of photosensitisation.

Photosensitisation as a means of killing or inactivating unwanted, or uneconomic, cells is far older than *Homo sapiens*, as there are various plants and fungi which use natural product photosensitisers to this end. For example, the flowering plant *Sanguinaria canadensis*, or bloodroot, exudes a milk containing sanguinarine, a photosensitiser which coats the cuticles of herbivorous insects, consequently causing photodamage in daylight (Arnason *et al.*, 1992). Conversely, the parasitic fungus *Hypocrella bambusae* uses condensed aromatic pigments called hypocrellins to photosensitise and break down plant cell walls (Diwu and Lown, 1994).

Man's use of photosensitisers has taken two main routes: anti-cancer and antimicrobial. Both of these were demonstrated during the first years of the twentieth century, but until recently were considered to be relatively unimportant in terms of clinical application. Photoantimicrobial action was demonstrated by Raab in 1900, who reported the inactivation of paramecia using acridine and eosin (Raab, 1900). Others, such as Tappeiner and Jesionek (1903), used similar dyes against neoplasms of the skin.

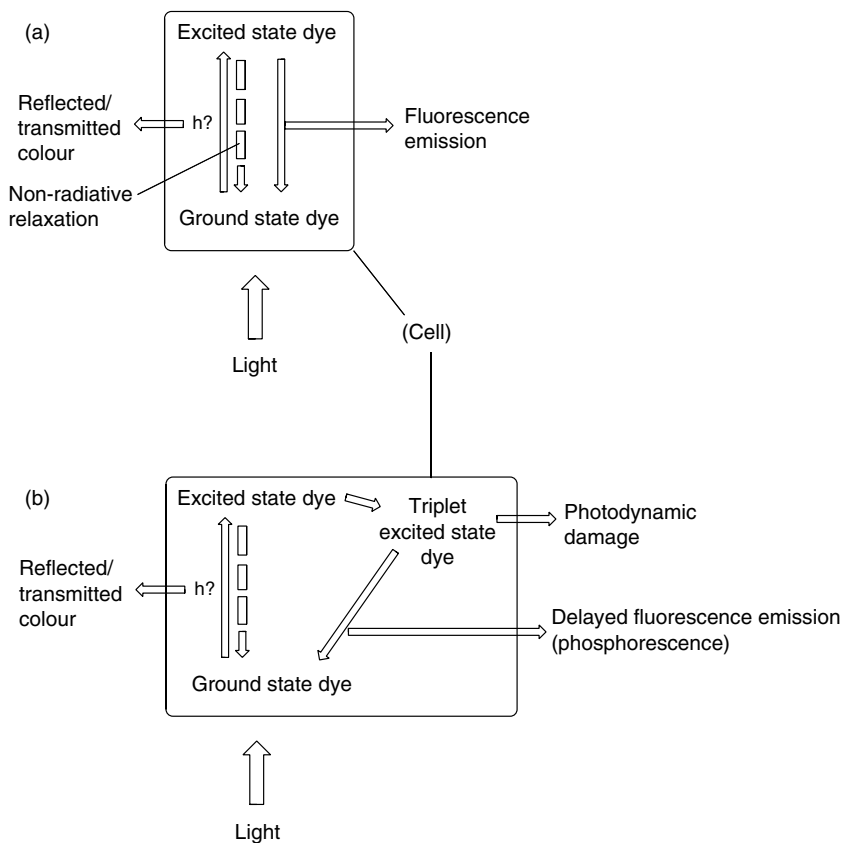
Whether used against microbial species, tumours or other unwanted human cells, the processes involving the electronics of the photosensitiser are the same, and are compared with other dye photoprocesses in Fig. 6.7. The existence of long-lived singlet and triplet states explains the different behaviour of photosensitisers on illumination, the triplet state being able to undergo redox reactions with the photosensitiser's environment or to transfer the excitational energy to *in situ* oxygen molecules, producing the highly reactive – and thus toxic – singlet oxygen.

6.5.1 Photodynamic therapy (PDT)

Due to early findings involving the fluorescence of natural porphyrin derivatives in cancers during surgery, much of the clinical application of photosensitisers – whether in the treatment of tumours of the skin, lungs, breast, brain, etc. – has been, and remains, porphyrin based. However, there were drawbacks associated with first-generation photosensitisers such as haematoporphyrin derivative (HpD) with regard to impurities, poor photoproperties and skin photosensitivity (Brown *et al.*, 2004). Subsequent synthetic candidates have been based on the phthalocyanine, phenothiazinium and cyanine dyes.

Phthalocyanines

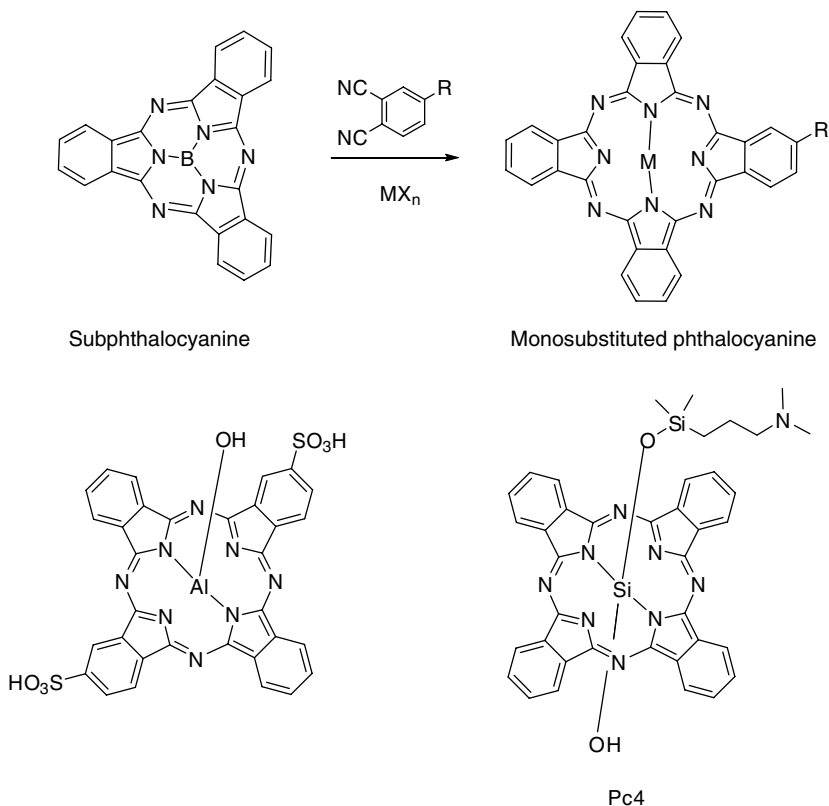
Given the structural similarity with the porphyrin nucleus, it is not surprising that phthalocyanines have been investigated by various groups worldwide as replacements for HpD and similar porphyrin types, particularly in view of the much more intense light absorption characteristics in the red and



6.7 Cellular dye photoprocesses. (a) Visible/fluorescent biological staining; (b) phosphorescent staining and photodynamic action.

near-infrared regions of the spectrum. However, although the dye chemistry associated with phthalocyanines is well established, it is based squarely on copper phthalocyanine, a very stable blue pigment. Unfortunately, due to its paramagnetic nature, copper (II) allows rapid deactivation of the excited singlet state and is thus a very poor photosensitiser. Consequently, diamagnetic derivatives were sought, such as those including a central zinc or aluminium ion.

In order to produce aqueous-soluble dyes, the phthalocyanine nucleus is often sulphonated, or produced from carboxylic acid-bearing starting materials. In practice, such approaches result in product mixtures and isomer formation which, although acceptable in the dye industry, is not suitable in drug development. Indeed, one of the arguments normally stated against the continued use of HpD concerns its lack of chemical purity. Nevertheless *Photosens* – a sulphonated mixture based on chloroaluminium



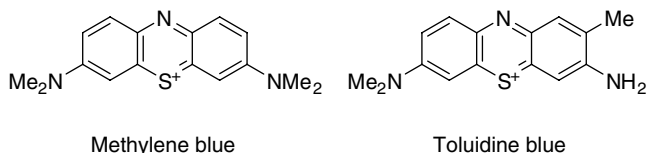
6.8 Phthalocyanines for use in photodynamic therapy.

phthalocyanine (e.g. Fig. 6.8) – has been licensed for use in the former Soviet Union (Filonenko *et al.*, 2008).

In order to circumvent the mixture/isomer problem, both monosubstitution has been reported, from phthalonitrile derivatives and subphthalocyanine (Fig. 6.8), as has functionalisation of the central metal/metalloid element. This last has been particularly successful using silicon, usually via the attachment of polar, basic/cationic chains (e.g. Pc4, Fig. 6.8), the resulting analogues having suitable properties and activities for both the anti-cancer and antimicrobial applications (Miller *et al.*, 2007).

Phenothiaziniums

Given the ubiquity of methylene blue (Fig. 6.9) in the present chapter, it is scarcely surprising to find that it is also involved in the development of drugs for PDT. The combination of low human toxicity and long use, coupled with an affinity for tumour tissue (see above) and its photosensitising activity have made it a key lead compound for both the anti-tumour and



6.9 Phenothiazinium leads.

antimicrobial approaches. A similar situation pertains with the related toluidine blue (Fig. 6.9).

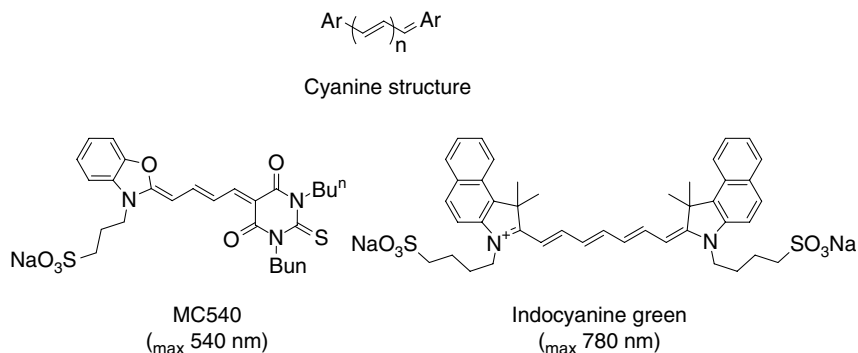
Early trials of these lead compounds for PDT reflected their hydrophilic nature – i.e. systemic administration leads to rapid elimination. Methylene blue has been tested as a photosensitiser in superficial bladder cancer (Williams *et al.*, 1989). Both the shape and hydrophilic-lipophilic balance of methylene blue have been varied by alteration of the auxochromic groups, either symmetrically or asymmetrically, to include greater hydrocarbon content – for example, the homologous series from methylene blue itself up to the bis(dihexylamino) derivative reported by Mellish *et al.* (2002). Such variation was shown to alter mammalian cell uptake and localisation, the derivatives not localising in the nucleus, thus circumventing much of the argument for potential mutagenic activity in human subjects. Both the symmetrical and asymmetrical derivatives – i.e. with respect to auxochromes – are readily prepared via bromine or iodine oxidation/amination methods, these being far less destructive to molecular structure than the originally used acid/chromium (VI) salts.

Cyanines

Fundamentally, cyanine dyes consist two heteroaromatic nuclei connected by an odd-numbered chain of linked methine ($-\text{CH}=\text{}$) units, facilitating the delocalisation of charge from one end to the other; the greater the delocalisation, the longer the maximum wavelength of absorption of the resulting chromophore (Fig. 6.10).

Given such simple structural requirements, cyanine dye analogue formation is relatively straightforward, e.g. via variation in heteroatom, *N*-alkylation, length of polymethine chain, etc., leading to the production of a large number of compounds. Despite this, there are very few examples of photosensitising drugs based on this class, being limited to merocyanine 540 (MC540) and indocyanine green (Fig. 6.10).

Merocyanine 540 is a lipid-soluble, anionic photosensitiser, these properties allowing it to pack into the outer leaflet of cell membranes, where there are low levels of anionic head groups (Matešik *et al.*, 2002). This has led to the use of MC540 in both the diagnosis and destruction of leukaemic cells relative to hematopoietic stem cells (Sieber *et al.*, 1984). The main current use of MC540 lies in the purging of leukaemic cells from fractions required for autologous bone marrow transplants (Chen *et al.*, 2000).



6.10 Cyanine examples.

Indocyanine green

As may be observed from Fig. 6.10, indocyanine green has an extended π -system compared to that of MC540. It has been noted above that the green dye is essentially non-toxic in humans, and this has led to various intraoperative staining applications. More recently this use has been extended into photodynamic areas, for example in the angiography of subjects treated for choroidal neovascularisation in age-related macular degeneration (Gomi *et al.*, 2008).

Although indocyanine green might be expected to act as a photosensitiser, it appears likely that observed effects are photothermal, rather than the traditional Type I/Type II photosensitisation routes covered above. The long wavelength band of indocyanine green, centred on the λ_{max} of 780 nm allows excitation by an 808 nm diode laser, and the excited cyanine then releases its excitational energy to its surroundings, causing thermal damage to cells (Chen *et al.*, 1995). The effect is still selective due to the required combination of chromophore localisation and light direction, although the approach may be employed in a less specific fashion to destroy tissue (photothermal ablation) (Diven *et al.*, 1996). A useful side product to this has been the use of indocyanine green in tissue soldering, as an alternative to suturing, the heat produced on illumination being used to increase the rate of reaction of added components, such as fibrin and albumin (Kirsch *et al.*, 1995).

6.5.2 Photodynamic antimicrobial chemotherapy (PACT)

Raab's original report (1900) of the photodynamic inactivation of paramecia is generally accepted as the starting point for photoantimicrobial research, while similar effects were shown in human tumours shortly afterwards. However, the subsequent pathways of the two related applications display a considerable disparity in reaching clinical reality. PDT, as noted above, is an

accepted clinical modality, whereas the antimicrobial application is still at the clinical trial stage. Much of the reason for this difference lies in the fact that there has been, from the late 1940s until relatively recently, a steady flow of clinically effective antibacterial agents. The problem of microbial – more particularly bacterial – drug resistance may be seen as the major driver in accelerating the clinical use of photoantimicrobial agents, in a similar way to the introduction of photodisinfective technology after the outbreak of the AIDS pandemic in the early 1980s.

As with PDT, photodynamic antimicrobial chemotherapy (PACT) is limited by the accessibility of light to the target, and to locally concentrated foci of infection. However, in terms of human disease, this still provides a considerable number of potentially amenable presentations. Indeed, owing to the much more rapid rates of microbial cell photokilling relative to that of human cells, it might be argued that microbial colonisation in any site of the body amenable to PDT may be eradicated effectively and rapidly using PACT. One mitigating factor against this is that there is a highly conservative attitude among the medical profession associated with conventional antimicrobial chemotherapy, although this must surely change with the continuously increasing rates of drug resistance. Secondly, the internal application of PACT represents an intervention, thus requiring an operational change for microbial disease.

The photosensitisers used in PACT – as with PDT – owe their regulatory approval to human safety rather than to outstanding photoantimicrobial action. Thus methylene blue has been licensed for use in oral photodisinfection, while it is clearly one of the weaker photoantimicrobial phenothiazinium derivatives (Wainwright and Giddens, 2003). It is also licensed for use in the photodecontamination of blood plasma (Wainwright *et al.*, 2007). There has been sporadic use of PDT-approved porphyrin photosensitisers in other presentations, such as virus-implicated papillomas (Wainwright, 2003a), and various clinical trials of newer photosensitisers, but progress towards proper clinical realisation remains torpid.

Despite the lack of clinical use, the desirable properties for effective photoantimicrobials are well appreciated – for example, the requirement for positive charge in conferring broad-spectrum antibacterial activity – i.e. against both Gram-positive and Gram-negative bacteria. It should also be noted that cationic photosensitisers retain such activity against bacteria, fungi, viruses and protozoa (e.g. the malarial parasite), and might thus be termed *pan*-spectrum antimicrobials.

6.6 Potential adverse effects of dyes

As the preceding sections have shown, dyes have a range of uses in the medical industry. The adverse effects of these dyes vary depending on the

particular use, the potential for human harm being generally governed by the type and duration of dye exposure. Thus, long-term intake of a given dye, for example in the diet, may be expected to have greater potential for harm than short-term external application of the same dye, for example as a superficial wound antiseptic. Wearing a garment dyed with the same compound would, logically, offer the lowest potential risk of harm.

Understanding the human toxicity of chemicals is generally complicated by the fact that *Homo sapiens* is such a complex entity. To have some idea of the problem, consider the following questions concerning the body: What is the toxic event? Where does this occur? How often must this occur to constitute toxicity? Is this always the same for every human? And for the chemical: Is this a pure entity? Is it altered by the metabolism? Plainly there are many variables possible, even arising from these few, basic questions.

There are also differences in the type of adverse reaction. Cellular toxicity (cytotoxicity) may occur either by a gross reaction (necrosis) such as protein precipitation, membrane destruction, etc., directly involving the chemical, or by a programmed route (apoptosis) involving the chemical in a primary event which then causes a stratified cascade of biochemical events, resulting in the shut-down of essential cellular machinery and inactivation. Mutagenicity involves the damage or other interruption of cellular DNA, resulting in its chemical or physical alteration and the subsequent incorrect copying of the base-pair templates and production of 'mutant' daughter cells. Carcinogenicity, the production of cells which exhibit uncontrolled growth, may be a consequence of mutagenicity, but not all mutagenic events lead to carcinogenesis.

Thus, when it is stated in the literature that a dye is toxic, this may cover a range of possibilities. In addition, the reader should be wary of toxicity studies based on single cell line investigations. Plainly the interaction of a dye with, for example, epithelial cells takes no account of the possible metabolism of the dye on its way to the target, nor of possible plasma protein binding and concentration effects. Similarly studies which show that certain dyes will bind to DNA or specific lipoproteins in isolation cannot absolutely reflect the situation in the body where, for example, a supposed mutagenic dye must reach the target organ, be taken up by a cell, locate the nucleus, cross the nuclear membrane and *then* interact with the nucleic acid – and all of this while remaining unmetabolised and unhindered by circulating biomolecules.

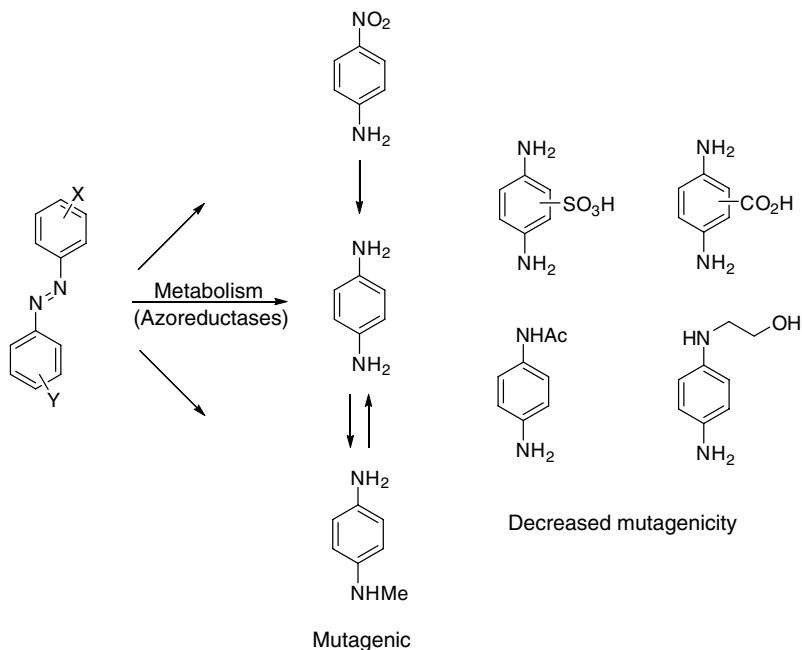
The production of novel compounds for use as drugs is a relatively straightforward proposition, as far as the chemistry is concerned. The difficulties usually arise once biological testing commences, and in particular in whole-animal screening studies (metabolism, pharmacokinetics, mutagenicity, etc.). Dyes for use in human medicine are subject to the same batteries

of tests and, once in the body, are exposed to the same metabolic pathways. This is covered in the following section.

6.6.1 Toxicology

To state that aniline is a toxic chemical is inexact. The metabolism of aniline produces several new chemicals which are toxic in various ways. However, the fact that anilines are widespread in dye synthesis produces the expectation that the metabolism of these dyes will result in aniline concentrations in the body. While this may be true in some cases, it does seem to be a 'blanket' attitude towards synthetic dyes in general. In addition, the modern understanding of metabolic pathways is such that the chemistry of aniline derivatives may be tailored to avoid such problems.

A simple treatment of azoic dye metabolism is given in Fig. 6.11. Obviously, the metabolites produced, typically by liver reductase enzymes in man, depend on the original dye molecule. However, it appears that *p*-phenylenediamine (1,4-diaminobenzene) is mutagenic, as are *N*-methylated derivatives and *p*-nitroaniline, which may be reduced to *p*-phenylenediamine (Chung and Cerniglia, 1992). Metabolites containing water-solubilising groups exhibit lowered potential mutagenicity, the increasing of xenobiotic hydrophilicity being one of the main outcomes of the metabolism, i.e. to



6.11 Potential azoic dye metabolites and mutagenicity.

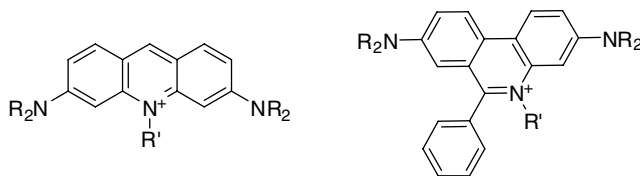
aid in elimination. It should also be remembered that dye molecules which are inherently hydrophilic are unlikely to remain in the human system for extended periods of time.

Dyes based on a simple *p*-phenylenediamine, or the related benzidine motif thus have strong arguments against their use in humans. However, many dyes contain the 1,4-diaminobenzene unit as part of a more complex structure without being mutagenic. For example, this unit may be seen in a high percentage of azine dyes. The lack of observed mutagenicity is due to the fact that the metabolism does not realise the discrete formation of *p*-phenylenediamine, usually due to maintained connection with another part of the azine ring system. Once again the hydrophilicity argument, with respect to rapid elimination, is relevant here.

6.6.2 Mutagenicity

Dyes which are known to interact with DNA are an obvious cause for concern where human use is intended. The prime example of this is provided by the acridine class. The affinity of aminocridines and the isomeric aminophenanthridines (e.g. ethidium bromide) for DNA has been shown to lead to mutagenic effects on bacteria and yeasts in culture (Hass and Webb, 1981). However, it is not certain whether these effects are transferable to humans, but it is likely that the case against acridines and phenanthridines (Fig. 6.12) is based on non-human, experimental data, and then only for a small range of compounds. While it is obviously impossible to trial such compounds for side effects in humans, there have been many people, especially in the services, who received aminoacridines in the first half of the twentieth century, either in antiseptics or as anti-malarials. If the potential for tumour expression is so high in such compounds, where are the data showing increased incidence of cancer among such people?

Mutagenicity caused by an intercalative mechanism requires a significant interaction between the DNA base pairs and the intercalator. However, the idea that intercalation requires a cationic, planar molecule of approximately acridine size is not necessarily correct. It has been shown that simple cationic character is insufficient, hydrogen bonding also being required. For



6.12 Acridinium and phenanthridinium intercalators ($R = H$, $R' = H$, alkyl) and non-intercalators ($R = R' = \text{alkyl}$).

example, whereas proflavine (acridine structure, Fig. 6.12, $R = R' = H$) is an effective acridine intercalator, at least *in vitro*, *N*-methyl acridine orange (acridine structure, Fig. 6.12, $R=R'=Me$) produces molecules which no longer intercalate. The related ethidium cation (phenanthridine structure, Fig. 6.12, $R = H$, $R' = Et$) behaves similarly (Zimmermann, 1986).

Adverse effects of dyes in the human system are plainly not straightforward and depend on many different criteria. In addition, dyes intended for use in patients, as has been mentioned, must be produced like pharmaceuticals, i.e. to ultra-high purity levels, since the range of impurities associated with ordinary textile dyes, for example, would raise the potential for toxic side effects considerably, particularly where the dyes are produced from simple aniline-type starting materials. Obviously, increasing knowledge of dye metabolism will aid in minimising risks to the patient.

6.7 Future prospects

As a class, dyes are the oldest of functional organic chemicals. This is underpinned by the growth out of dyestuffs of biological stains and then drugs. There is thus a wealth of experience and a concomitant permanent record pertaining to dye chemistry and action. This is often forgotten in the constant scientific push for new ideas. Without a basis in historical fact, 'new' ideas are often found to have been tried previously, and presumably unsuccessfully. The point of such an argument is not to encourage the reintroduction of earlier materials and technologies, but to promote awareness of what has gone before in terms of research patterns and approaches to similar problems (infection control, for example).

The common perception of the medical industry is of one of the more go-ahead, forward-looking concerns, constant breakthroughs occurring in disease treatment or management, particularly from the point of view of technological miniaturisation, increasing rates of diagnosis and cutting morbidity and mortality via screening programmes. Dyes should continue to play an important part in this, mainly in the provision of evidence of disease via biological stains, tracers or molecular probes.

Both dye toxicity and tissue colouration remain obstacles to the use of dyes and their derivatives in humans. This is as much due to the health-care perception of dyes as 'old technology' as it is to toxicological data. Thus whether dyes are used to colour our medicines or to constitute them directly – as conventional or photodynamic therapeutics – will depend on proper, non-biased cost-benefit analyses. Hopefully, the benefits already demonstrated by thousands of photodynamic treatments in cancer patients will allow this particular discipline to flourish, and there is no doubt that microbial, especially bacterial, drug resistance offers an enormous potential field for the application of photoantimicrobials. For both the anti-cancer

and antimicrobial approaches, however, there remains the human toxicity hurdle and the future, expanding use of photosensitisers depends on how well navigated this is. The technology and expertise are in place. It remains to be seen whether or not government and healthcare concerns are willing to make the leap.

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B. KAUR and S. N. BHATTACHARYA, RMIT University, Australia

Abstract: This chapter discusses various issues of dyes and pigments and different types of pigments used for automotive applications. It also highlights the different techniques used to improve the performance of pigments such as chip resistance, mechanical strength and reduction in Environmental impact. The chapter concludes with different methods of application of dyes and pigments and the future trends in the automotive industry.

Key words: automotive, chip resistance, environmental impact, techniques.

7.1 Introduction

Automotive industries consume a large amount of high performance pigments and dyes. Pigments are preferable to dyes because dyes do not have sufficient light-fastness required for automotive applications. Inorganic, organic, special effects pigments and functional pigments are the major categories of pigments used in automotive industry. The quality requirements for automotive pigments, particularly for exterior coating applications, are significantly higher than those for other applications.

This chapter deals with key issues of dyes and pigments encountered in the automotive industries which include excellence in performance, long-term durability, compatibility with health, safety and environment, cost effectiveness and consumer demands. Important properties of pigments to be discussed are chip resistance, corrosion resistance, weather resistance, light-fastness, thermal stability and bleeding resistance. Techniques for the production of key pigments to enhance their performance such as calcination, pigment conditioning and surface treatment are also highlighted.

Application of dyes and pigments will be focused on paints and coatings for the exterior as well as the colouration techniques for interior polymeric components of automobiles. Although high performance pigments such as cadmium-based pigments and lead-based pigments are currently in wide use, but due to their toxicity and environmental issues these might need replacement by other environment friendly pigments such as rare earth cerium

sulphide, bismuth vanadate and organic pigments.¹ The chapter ends with a discussion of the future trends of pigment use for automotive applications.

7.2 Key issues of automotive dyes and pigments

7.2.1 Performance capability

The aesthetic look and colour of cars are very important to customers. Some customers decide the brand and model of their car depending upon the availability of colours in that brand. The popularity of colours changes with time; for example metallic pearl scent colours are becoming more popular these days over the flat colours. The BASF report on colour trends (7 April 2008) clearly indicates that colours with special effects especially white pearl, silver, red, blue and black colours are customers' top five favourite colours. To keep the aesthetic look long-lasting, pigments used in automobiles need to possess high heat resistance, light-fastness, weather stability and bleeding resistance. Besides the aesthetic look, dyes and pigments have to show performance capability in regard to their processing and full visual effect. The required technical properties include rheological behaviour, flocculation, sedimentation, storage behaviour and ability to disperse in vehicle media.^{2,3}

7.2.2 Functionality of dyes and pigments

Functionality of a pigment is decided based on its area of application. Dyes and pigments serve different functions depending on whether they are used in primer coating or in top coatings. For example, functions such as provision of high mechanical strength, corrosion resistance and chip resistance become more important than colour if a pigment has to be used in a primer coat. For this reason carbon black and white titanium oxide pigments are commonly used in primer coats. In addition to these pigments, extenders such as barium sulphate, talc, feldspar and other additives (which are discussed in more detail in Section 7.3.4) are added to the primer coat to improve their performance.

On the other hand for the pigment to be used in top coat, its colour, aesthetic look and its visual effect are of prime importance along with other performance characteristics.³ To improve the aesthetic look and visual effects, blending of traditional pigments with special effects pigments such as metallic effect and pearlescent pigments is a common practice these days (different categories of special effect pigments are discussed later). For organic pigments functionality, especially their colour characteristics, also depends upon the functional group. This is well illustrated by isoindolinone pigment, a yellow coloured pigment, which in chlorinated form – tetrachloroisoindolinone

pigment – comes in different shades from yellow and orange to red and brown. In this case bathochromic shift is observed by introduction of chlorine atoms due to the donor–acceptor complex, where amine functions as a donor and the tetrachlorinated nucleus acts as acceptor.⁴ A similar phenomenon is observed in perylene pigments where different colours result from the different extent of overlap between adjacent perylene molecules in their crystal structure.⁵

In addition to the above stated standard functions for a colourant in the automotive industry, there is always demand to achieve extra functions from a given colouring material. This includes development of cool coatings to reduce heat build-up in automobiles while keeping their aesthetic look. This is achieved by selective use of pigments which absorb strongly in the visible region to give a visual appearance of dark colour but reflect significantly in the NIR (near infrared) region of the solar spectrum to reduce extra heat gain. This has been reported in coating development where the primer coat involves the use of titanium dioxide pigments (strong NIR reflector) and the top coat involves the use of NIR-transparent pigments such as perylene pigments to give that coating the visual appearance of dark colour.⁶ More recently PPG patented a coating composition in which perylene-based pigments are blended with special effects pigments to achieve dark colour coatings with special visual effect along with the control of heat build-up.⁷

7.2.3 Environmental impact

Although pigments do not seem to have any environmental impact directly, indirectly heat absorbing pigments (especially dark coloured) result in considerable heat build-up. Air conditioners are run to reduce the discomfort of heat which impact the environment in two ways.⁸

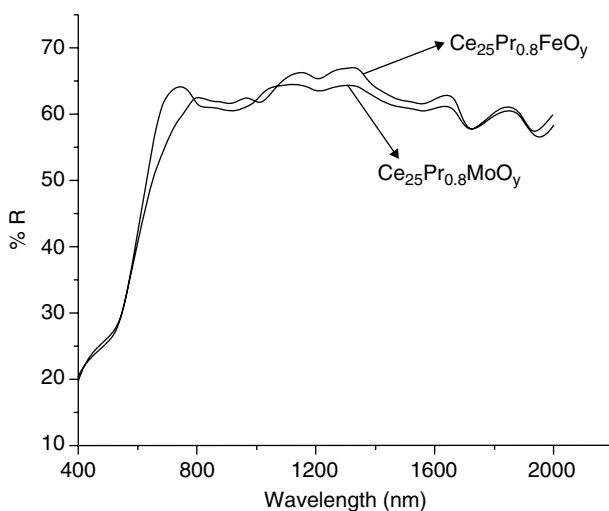
1. Air conditioners are major sources of chlorofluorocarbons (CFCs).
2. Air conditioners result in more consumption of fuel energy which releases more CO₂, thus contributing towards greenhouse gas build-up in the atmosphere.

Cool pigments which absorb strongly in visible region but reflect significant amount of NIR radiation of solar spectrum are good alternatives to reduce the environmental impact. For this reason more research is performed these days to enhance the appropriate properties of these pigments. NIR reflectance or NIR transparency has been observed to be an important property to distinguish cool pigments from traditional pigments. Recently Levinson studied the reflectance of 87 different pigments (which include organic as well as inorganic pigments) in the NIR region to distinguish cool pigments

from traditional pigments.⁹ Similar research on rare earth metals has led to them being categorised as cool pigments. Figure 7.1 shows the percentage reflectance of rare earth metals for general formula $Ce_{2.5}Pr_xTm_yO_z$ (where Ce = Cerium, Pr = praseodymium, Tm = transition metal, O = oxygen) in the NIR region. These pigments have exhibited 70–80% reflectance of solar radiations in the wavelength region of 1000–2200 nm.¹⁰ The use of such pigments can help to reduce the environmental impact by reducing heat build-up.

7.2.4 Toxicology of pigments

In regard to laws and regulations, the toxicity of pigments is fast becoming a major issue for their use. This issue is of major concern for inorganic pigments as many of inorganic pigments which are based on heavy metals are toxic. The rules governing toxicity have affected the use of lead-based pigments and cadmium-based pigments. In spite of having high degree of pigment performance qualities, such as brilliant colour, excellent light-fastness, weather stability, thermal stability and good ability to disperse, these pigments face reduction in their use due to associated toxicity. On the other hand pigments like bismuth vanadate which can give brilliant colours like cadmium pigments but are relatively non-toxic are gaining more importance.¹¹ Organic pigments which are not associated with any toxicity due to their low solubility in water might become more popular in the future.



7.1 NIR-spectrums of $Ce_{25}Pr_{0.8}FeO_y$ and $Ce_{25}Pr_{0.8}MoO_y$. (Adapted from Sreeram *et al.*,¹⁰ p. 1466.)

7.3 Major pigment types used in automotive coatings

A list of different pigments and their subclasses with important characteristics which make them suitable for automotive application is given in Table 7.1. Pigments used in the automotive industries can be broadly classified into the following categories:

- Inorganic pigments
- Organic pigments
- Special effects pigments
- Functional pigments.

7.3.1 Inorganic pigments

There is a long list of inorganic pigments but only the pigments used in automotive applications and their characteristics which make them suitable for automotive finish are discussed in this section.

Cadmium pigments

Cadmium pigments exhibit a wide range of vivid and bright red, orange and yellow shades along with excellent heat stability, light-fastness, weather resistance, chemical resistance, non-bleeding characteristics and good dispersibility. Yet their use in automotive applications accounts for less than 1% of their production. The toxic nature of these pigments is a major disadvantage of their use.

Bismuth vanadate

Bismuth vanadate pigments show colouristic properties similar to that of cadmium yellow and lead yellow. They offer brilliant greenish yellow to reddish yellow shades with excellent performance capability as well as good dispersibility in aqueous medium and non-aqueous medium. All these characteristics and their non-toxic nature make them suitable for use in coatings for automotive finishes.

Rare earth sulphides pigments

In the category of rare earth sulphides pigments cerium sulphides are the most common. These pigments have excellent colouristic properties which are either similar or superior to cadmium pigments and lead molybdates. They also possess all the properties required for automotive application

Table 7.1 Different pigments used in automotive applications

Main class of pigment	Subclass of pigment	Colour and other important characteristics
Inorganic pigments	Bismuth vanadate	Brilliant greenish yellow to reddish yellow, high colour strength, good hiding power, good light- and weather fastness, excellent dispersibility and no toxicity issue.
	Cadmium pigments	Bright colours ranging from yellow to red with different shades, high thermal stability, good light and weather fastness, chemical resistance and ability to disperse in vehicle medium.
	Lead pigments	Bright colours, high tintorial strength, high hiding power, good dispersion, excellent thermal and light stability.
	Rare earth sulphide pigments	Bright colours ranging from red to yellow with high tintorial strength, excellent light and weather fastness, good chemical resistance, ease to disperse, high NIR reflectance and non-toxic.
	Opaque/transparent red iron oxide (PR 101) and yellow iron oxide (PY42)	PR 101 (α -Fe ₂ O ₃) is red and PY 42 (α -FeO(OH)) is yellow in colour. Both pigments show high hiding power, resistance to alkalis and ease to dispersion with no toxicity issue.
Organic pigments	Perylene pigment	Bright red colours, high tintorial strength and colouring power, excellent thermal and light stability, good weather fastness, non-toxicity and transparency in NIR region.
	Tetrachloroisindolinone	Bright yellow shades, resistance to acids, good heat, light and weather stability, good chemical resistance and non-toxic.
	Isindoline	Wide range of colours from greenish yellow, reddish, orange and brown and no toxicity issue.
	Benzimidazolone	Bright greenish yellow colour with outstanding light and weather fastness, good chemical resistance and good flow properties with non-toxic behaviour.

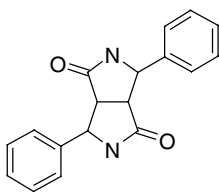
Quinacridone	Range of colours from golden to violet, excellent photo stability and weather resistance, high thermal resistance, easy to disperse in water and organic solvent, no toxicity issue.
Diketo-pyrrole	Colour varies from red to bright orange, good hiding power, excellent fastness to solvents, weather and light, good heat stability and ease to disperse in aqueous medium along with low environmental impact.
Dioxazine	Pigments PV 23 from this class offer high intense blue colour with good hiding power.
Aluminium flakes	Special aesthetic look and visual effects along with high thermal stability,
Iron oxide coated aluminium	Ability to blend with other pigments to create variety of special effect
Pearlescent pigment	pigments and no toxicity.
Colour variable pigments	
Graphitan pigments	
Titanium oxide	
Barium sulphate	All these functional pigments are white except carbon which is black. High mechanical strength, chip resistance and corrosion resistance make them useful in primer coats of automobiles.
Talc	
Silicon dioxide	
Feldspar	
Carbon blacks	

such as excellent dispersibility, light-fastness, weather stability, heat resistance, non-toxicity and low environmental impact. The ownership of the last two characteristics puts them at a higher grade to cadmium pigments and lead-based pigments.

7.3.2 Organic pigments

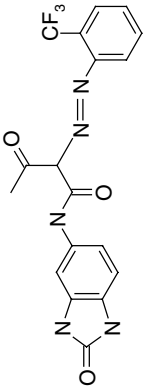
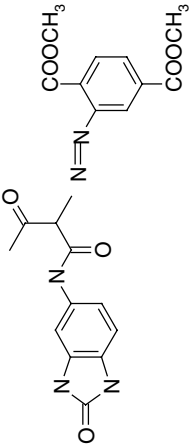
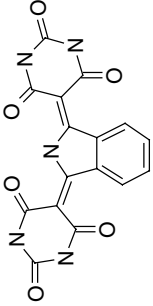
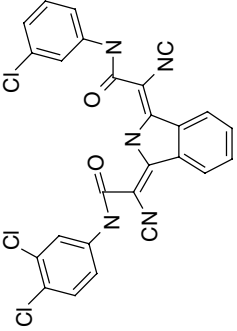
Nearly 50% of the total production of organic pigments is used in automotive applications. Organic pigments outclass inorganic pigments in regard to toxicity as the majority of organic pigments have either no or very low toxicity. The major classes of organic pigments which are in use in automotive coatings include perylene, benzimidazolone, isoindoline, isoindolinone, quinacridone, diketopyrrolopyrrole, dioxazine and phthalocyanine pigments. There are many dyes and pigments reported in each class but very few of them meet the automotive standard. Different classes of organic pigments and commercialised pigments of automotive standard of each class along with their chemical structure and manufacturer are listed in Table 7.2.

Rather than dealing with detailed synthesis of these pigments, which has been discussed in earlier literature, this section deals with the structures of important organic pigments which make them suitable for automotive finishes. One major feature of the organic pigments is that they offer a wide variety of colours in comparison to inorganic pigments which have a limited range of colours. This is attributed to the creation of a large variety of colours by different substitution patterns and polymorphism. Pigment PV 19 of quinacridone class exists in three polymorphic forms α , β and γ . The beta form exists in violet colour whereas alpha and gamma forms are red in colour. Pigments PR122 and PR202 belong to same organic class with different nature of substituent at positions 2 and 9. This results in a variation in the colour from red to magenta. A similar phenomenon is observed in isoindolinone pigment where chlorination of these pigments results in a variety of shades from yellow and orange to red and brown in comparison to yellow coloured parent pigments. Diketopyrrolopyrrole pigment (PR254) is red in colour which represents dichlorinated product of pigment PR 255



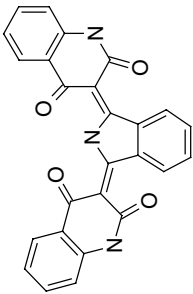
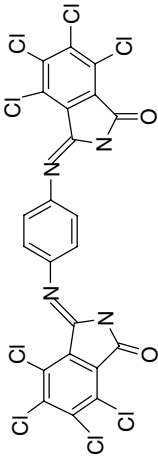
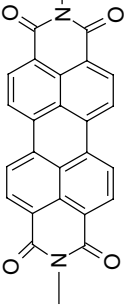
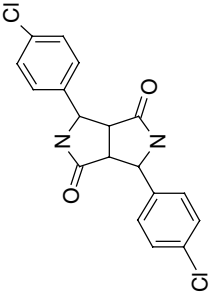
7.2 Pigment PR 255.

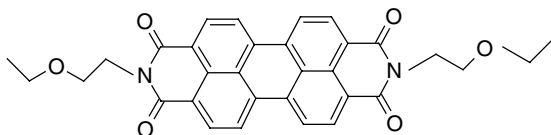
Table 7.2 List of organic pigments used in automobiles, their chemical structure and manufacturers

Main class of pigment	C.I. Pigment No.	Chemical structure	Manufacturer
Benzimidazole pigment	PY 154		Clariant Intern. Ltd., CH
	PY 175		Clariant Intern. Ltd., CH Dainichisoka Color & Chemicals, JP
Isoindoline pigments	PY 139		BASF
	PO 66		CIBA

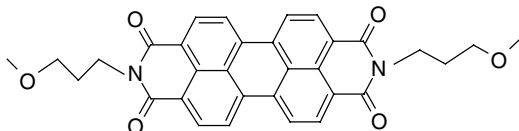
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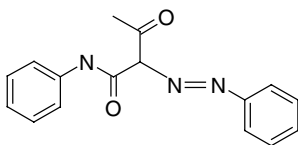
Main class of pigment	C.I. Pigment No.	Chemical structure	Manufacturer
	P.Br. 38		BASF
Tetrachloroisoindonone	PY 110		BASF
Perylene pigments	PR 179		BASF, Sun Chemical, CIBA, BAYER
Diketopyrrolopyrrole pigments	PR 254		



7.3 3-Oxapentylperylene.



7.4 4-Oxapentylperylene.



7.5 Monoazo yellow pigment.

(Fig. 7.2) which is yellowish red in colour. Perylene pigments are also known to exhibit pronounced effect on colour with small change in the nature of substituent. For example moving the oxygen from position 3 in the side chain of 3-oxapentylperylene (Fig. 7.3) to position 4-oxapentylperylene (Fig. 7.4) results in a dramatic colour change from red to black.

Introduction of different substituents can help to improve the migration fastness in organic pigments. This is well illustrated by benzimidazole. These pigments are produced by the introduction of five-membered heterocyclic rings to benzene nucleus of monoazo yellow pigments (Fig. 7.5). Benzimidazole pigments are much superior to Monoazo yellow pigments in terms of migration fastness owing to their ability to form intermolecular hydrogen bonding which results in decrease in their solubility in solvents.

7.3.3 Special effects pigments

Special effects pigments are gaining increasing popularity in automotive coatings because of their brilliance and special visual effects along with their outstanding weather resistance and no toxicity. These pigments fall into the following major categories:

- Pearlescent and interference pigments
- Metallic effect pigments.

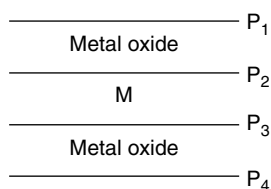
Pearlescent and interference pigments

These pigments can further be classified as oxide coated metal platelets, oxide coated mica platelets, oxide coated silica and aluminium flakes, platelet-like monocrystals and liquid crystal polymer platelets. All these pigments consist of alternating transparent layers with different refractive indices. The interplay of colours is produced by these pigments due to the layered structure of metal oxide, which is responsible for the rich, deep glossy effect¹² and helps them to simulate pearl lustre. Different effect pigments used in automotive applications and their manufacturers are listed in Table 7.3.

Figure 7.6 illustrates a typical three-layered pearlescent pigment where the central layer M (M = metal, mica, silica, aluminium) is sandwiched between two metal oxide layers. This results in three layers with different refractive indices and four phase boundaries P_1 – P_4 . Interference of light is generated by reflection of all the six combinations of phase boundaries P_1P_2 , P_3P_4 , P_1P_3 , P_2P_4 , P_1P_4 and P_2P_3 . This interference effect depends upon the

Table 7.3 List of some commercial special effects pigments used in the automotive industry and their manufacturers

Pigment category	Commercial name	Manufacturer
Pearlescent pigments	Afflair 30719307 Stargold	EM Industries, Howthorne, NY
Metal oxide coated silica flakes	'Colorstream'	EM Industries, Howthorne, NY
Coated aluminium oxide pigments	'Xirallic crystal silver'	EM Industries, Howthorne, NY
Multiple layer effect pigments	'Chromaflair'	Flex, BASF
	'Variochroma'	
Liquid crystal effect pigments	'Helicone'	Wacke
Light diffractive pigments	SpectraFlair Diffractive pigments SecureShift Pigments	Flex



7.6 Diagrammatic representation of a pearlescent pigment (M = Metal flakes, mica, silica flake, aluminium flakes, liquid crystal polymer, etc.).



7.7 Typical metallic flake-based paint.

thickness of the upper and lower metal oxide. Iron oxide, aluminium oxide and titanium oxide are the most common metal oxides used to create pearlescent pigments.

Metal effect pigments

Metal effect pigments consist of very thin metal flakes or wafers which act as tiny mirrors as shown in Fig. 7.7. The metallic effect is caused by the reflection of light at the surface of the metal particle. In these pigments, lightness depends on the observation angle and this phenomenon is called lightness flop. Aluminium flakes are the most commonly used in automotive applications for the following reasons.

1. Silver cars have been the most popular for several years and account for one third of total production in 2006.³
2. High thermal performance.¹³
3. Aluminium flakes are used in combination with other pigments to create many other special effects pigments.

However, with the evolution of this technology coatings containing aluminium pigments were applied at much higher shear forces. This produced a dull metallic effect to the final finish. Recent advances have overcome this problem by developing shear-resistant pigments to maintain both high brightness and metallic effect.

In addition to aluminium flake effect pigments, iron oxide coated with aluminium, colour variable pigments and graphitan pigments are also common in the automotive industry.

7.3.4 Functional pigments

The functional pigments category includes all the extenders and pigments used to enhance performance capability and functionality depending upon their application. Their main application lies in the improvement of hiding power, corrosion resistance, chip resistance and other rheological properties of primer coats. Mainly black and white pigments are used for this purpose as colour is not as important for the primer coat as for the top coat. The main pigments and extenders to serve this purpose in primer coat include titanium oxide, barium sulphate, talc, silicon dioxide, feldspar, carbon black and additives.

Because of high density $4.1\text{--}4.2\text{ g cm}^{-3}$ and high refractive index of titanium dioxide, its addition helps in providing a good hiding power whereas its hardness value provides good chip resistance.

Barium sulphate also has high density of 4.1 g cm^{-3} but owing to its low refractive index it has no contribution to hiding power. Due to its low cost it is used as extender to fill the space to improve hiding power in dispersion with titanium oxide.

Talc is used to adjust the fracture properties of the primer surface. A good balance between adhesion and cohesion is essential to achieve good chip resistance. Talc helps to improve chip resistance by converting adhesion fracture into cohesion fracture.

Silicon dioxide affects the rheology of the coating material. It is used as a matting agent for obtaining matt surfaces.

Feldspar is an aluminosilicate and has relatively high hardness. It is used as an extender and is good in adjusting the sanding properties of primers.

Carbon black is used when greater colour depth is required because of its high absorption of light.

As far as top coats are concerned certain categories of special effects pigments (discussed above) are mixed with other different coloured pigments to obtain a specific visual effect.

7.4 Techniques commonly used to improve the technical performance of pigments

There are various methods for enhancement of the performance capability of a pigment after its production. The method to be adopted depends on the required property enhancement for the pigment. A few of these methods are described below.

7.4.1 Calcination

Calcination is a process of heating a substance under controlled temperature and in a controlled environment. This process is known to improve the chroma, tinctorial strength, pigmentary texture, weather stability, light-fastness and thermal stability of pigment whereas it has adverse effect on the dispersibility of pigments. Calcination is an important step in the manufacture of cadmium pigments to achieve particular pigmentary characteristics. In the production of cadmium pigments, temperature of calcination, residence time and calcining atmosphere influence the colour and pigment texture. Lower calcination temperature results in lighter and brighter pigment shade but with less strength whereas higher temperature results in deeper shade. This process plays a vital role for the titanium dioxide pigments as well.

Calcination is not just confined to inorganic pigments; organic pigments can also be calcinated to improve their performance. One recent example of this is the enhancement in the blackness weather fastness and heat resistance in perylene black pigment.¹⁴

7.4.2 Surface modification of pigments

Environmental legislation forces paint makers to reduce the emission of volatile organic compounds (VOCs) in paint. Reduction in the solvent level in coatings is an effective and attractive way to reduce the release of VOC into the environment. This poses another challenge of proper dispersion of extra pigment to achieve stable viscosity and aesthetic appeal of automotive finish. Modification of the pigment surface and use of appropriate polymeric dispersant have been observed to have a significant influence on the viscosity and dispersibility of pigments. This is well illustrated by surface modification of diketopyrrolopyrrole pigments PR254, PR264 where surface modification along with the use of different polymeric dispersants such as Solsperse 32600 and EFKA-4060 has reduced the viscosity of the liquid system considerably.¹⁵

7.4.3 Pigment conditioning

Conditioning of pigments is a common practice to improve the colouristic, physical and application-specific characteristics of pigments. For conditioning, the crude form of pigments is given some special treatment to achieve adjustment in particle size, size distribution, surface charge of pigment, pigment morphology, pigment wettability and stability.

7.4.4 Addition of sagging control additives

As metallic effect colours are more popular in cars, it is worth discussing the role of anti-sagging agents to achieve full colour strength. Orientation of flakes is strongly influenced by the rheology of paint. Poor flake orientation due to sagging results in poor colour development. Addition of rheology control agents such as micro gel, wax dispersion and urea based anti-sagging agent is commonly used in solvent-based coatings. The crystals of urea type addition product of benzylamine and hexamethylene diisocyanate are common sagging control agents in solvent-based coatings.

7.5 Application technology

Paint is applied to cars in three layers: primer coat, base coat and top coat.

7.5.1 Primer coat

As stated earlier, primer coat serves the purpose of providing chip resistance, mechanical strength and substrate hiding. Titanium dioxide and carbon black are common pigments along with extenders and additives to achieve required performance. As far as the application is concerned, primer coat is applied in liquid form as well as in powder form.

The principle for the application of liquid primer surfacer is that it is atomised in air and transferred to the metal. The following spray application methods are used

- Single-substance nozzles – airless application
- Dual-substance nozzles – pneumatic application
- Pneumatic atomisation – electrostatic charging
- Centrifugal atomisation – electrostatic high rotation.

Electrostatic high rotation is a preferred method of application of primer surfacer as it provides optimum atomisation and transfer efficiency in comparison to other methods.³

In the powder form of primer surfacer, the first step is the manufacture of it which involves weighing of base materials and premixing of these materials. Pigments are dispersed in the continuously working extruder. The friction energy imparted by the warm screw is so high that it melts the binder and pigments are wetted in the molten mix. After leaving the extruder, the molten mix is rolled out and cooled. This is followed by breaking of the mix into small chips and grinding to fine powder.

The particle size distribution is an important factor to optimise the flowability of powder primer. Particle size $\leq 60\mu\text{m}$ can provide optimum flowability.¹⁶ The standard method of applying the powder primer involves fluidisation of the powder to make it pneumatically transferable. Air is blown through the porous floor of a tank to generate a swirling vortex of powder called the fluidised bed.

7.5.2 Base coat

The base coat gives colour to cars and is applied over the primer coat. There are three base coat systems used in the automotive industry worldwide:

- Medium solids
- High solids
- Waterborne system.

The medium solids base coat system contains 25–40% of solid matters for solid colours and 15–25% for effect colours. This system is the least used and is being replaced by high solid systems in which 45–60% solid matter is used

for solid colours and 40–50% for effect colours. This transition is intended to reduce the emission of VOCs in response to Environment Protection Agency (EPA) regulations. The major drawback of this system is that it is more susceptible to sagging which is overcome by the use of anti-sagging agents.

The waterborne base coat system was first introduced at industrial level in 1987 and gained popularity in Europe after 2000.³ Japan and Germany have totally converted to the waterborne base coat system whereas the high solid system is still the most popular method in North America. Developing countries like China, Korea and Brazil are also transferring to this system. The main reasons for the popularity of this system is the significant reduction in the emission of VOCs in comparison to other systems and greater control of rheology which results in better colour development.

For the application of base coat, the car body first passes through an EMU station for dust extraction, followed by base coat application to interior areas either manually or by robot application. This is followed by base coat application to the car externally by electrostatic bell application. For solid colours only a single layer of the base coat is applied whereas for effect colours a second base coat layer is applied by pneumatic spray or by second electrostatic bell application.

As special effects colours are gaining popularity in automotive industry, it is worthwhile to mention that for effect colour shades, orientation of metallic or mica flakes parallel to the substrate control the lightness difference, which is a flop between the perpendicular and inclined observation angle. Different effects can be created using different spray methods, e.g. the effect created by pneumatic spray is different to that created by electrostatic spray. The difference is due to difference in orientation of flakes in the base coat. This factor becomes very important for colour matching in case of car repairs. In general, electrostatic bell application results in poor flake orientation which is attributed to the fact that it is less wet and droplets have relatively less momentum when reaching the substrate. Another factor which controls flake orientation in effecting colour shades is rheology of the paint. Rheology control agents, which have already been discussed as sagging control agents, are added to achieve good flake orientation.¹⁷

7.6 Future trends in automotive pigments

The automotive industry has gone through a dramatic change in colour trends and performance capability, as well as methods of application of colours to automobiles. These changes are in response to the customer demand for different colours. The focus is to achieve long-lasting performance of given pigments, with lower cost and environment impact in addition to considering the toxicity of a given pigment.

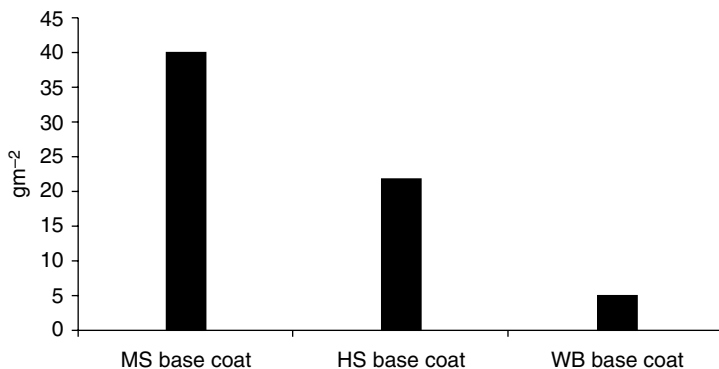
Laws and regulations regarding the legal limits of pigments are beneficial for some pigments whereas they have adverse affect on the demands for other pigments. For example, demands for lead-based and cadmium-based pigments have decreased in response to their toxicity issue. On the other hand rare earth metal based pigment, bismuth vanadate pigments, special effects pigments and organic pigments have shown increased demand in automotive applications. In regards to change in the trends of customers' colour choices special effects pigments have gained top popularity over the last few years.

In the 1970s, silver metallic effect pigments based on aluminium flakes were very popular for cars, followed by developments of pearl lustre such as Iriodin pigments, which created an elegant gloss on vehicles. In the 1990s colourstream pigments were developed for the automotive market. These are multi-colour effect pigments whose colour changes with viewing angle. This story of changing colour trends does not stop here, however. New Xirallic crystal silver pigments, which combine diamond-like sparkle with distinctive silver colour, are now gaining in popularity.¹⁷

According to one recent article¹⁸ FIREFLAKE pigments are expected to gain popularity over the metallic effect pigments. FIREFLAKE pigments are produced by bonding colourant to aluminium particle surface by a patented process to produce a single pigment. These coloured aluminium flakes combined with other pigments produce coatings that exhibit colour travel, or flop, when viewed from various angles. The better rheology and excellent hiding power of these pigments are other factors behind the popularity of these pigments.

In addition to the visual appearance of pigments, their environmental impact has become an important issue in recent years. For this reason organic pigments are always a pigment of choice for automotive applications as they offer brilliant colours, excellent hiding power, good tinctorial strength and high photo and weather stability. In addition, they have low environmental impact and no or very low toxicity associated with them. For this reason research on blending of special effects pigment with high performance organic pigments is on the rise to achieve multi-purpose function. A recent patent by PPG is a good example of this. NIR-transparent perylene-based pigments are blended with special effects pigments to develop coating for automobiles which can control heat build-up and hence reduce the impact on the environment while giving special visual effects to satisfy customer demand.⁶

Techniques of application of coatings have also undergone rapid change to achieve long-term performance, low cost and reduction in the release of VOCs. Manual painting techniques have been completely replaced by automated robot process which helps reduce imperfections and painting time significantly. Another aspect is reduction in organic solvent in coatings which forced coating technology to advance from medium solid coatings



7.8 Contribution (gm⁻²) to solvent emission from base coat in automotive coatings.

(MS) to high solid coatings (HS) and finally to waterborne coatings. This results in a significant reduction in VOC emission.

Waterborne base coat technology has resulted in the reduction of VOC emission by 35 gm⁻² compared to medium solid base coat technology as shown in Fig. 7.8. As a result, Germany, Japan and other countries in Western Europe have already changed completely to waterborne coating systems and the USA, China, Korea and Brazil would change to waterborne technology in the near future.³ In order to achieve reduction in environmental impact, the film thickness of auto-coating has been reduced to 100–140 µm and the number of layers of coating has also been reduced.

In the last 25 years the development of pigments with a high performance profile and low environmental impact in combination with improvement in their application techniques has resulted in coatings with enhanced corrosion protection and long-term durability of colour and gloss, while the environmental impact has reduced dramatically. This process of changing trends in colours and application techniques is likely to continue.

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A. P. DAMANT, Food Standards Agency, UK

Abstract: A general review is given of major substances currently used to colour food within the UK and the EU along with a short resumé of methods of analysis and a discussion of supporting legislation. Substances are classified as being either synthetic or natural dyes and the review provides information on food products in which the dyes can be used as well as highlighting any stability issues.

Key words: food, colours, dyes, analysis.

8.1 Introduction

Consumers require foods that are attractive and appetising. Such psychological factors stimulate the appetite and digestive system and contribute to the enjoyment of eating and drinking. Colour is often associated with quality. For example, green tomatoes and bananas would be rejected by consumers as being unripe solely because they are coloured green. The colour of food also contributes to recognition and flavour identifications, particularly in products which would otherwise be colourless (e.g. boiled sweets, ice cream and soft drinks).

Many foods are seasonal products and as such are subject to variation in colour (e.g. dairy products). Such colour variation can be minimised by adding food colourants to the product to produce a uniform material, all year round. The main reasons for adding food colourants to foods are:

- to restore natural colour lost during processing and storage;
- to reduce batch-to-batch variation of products;
- to supplement the intensity of natural colours where these are weak;
- to impart colour to otherwise colourless products; and,
- to produce acceptable and attractive products for the consumer.

Although most foods are coloured, the addition of colouring matter to foods is not a recent invention. The link between a consumer's appreciation

of a food and the food's appearance has been known for centuries. For example, the Toltec Indians of Latin America used cochineal as a colouring in the tenth century AD. Until the middle of the nineteenth century, the only colouring matters available were those derived from natural sources. From the twelfth century onwards, within the UK people delighted in the rose and violet coloured sugars imported from Alexandria. The colouring matters used were most probably Madder and Kermes, each giving a red shade, and Tyrian purple.¹

In 1856 the modern synthetic dyestuffs manufacturing industry was born, beginning with Sir W. H. Perkin's Mauve (Aniline Black), synthesised from coal-tar starting materials. Although these 'coal-tar' colours were initially intended for the textile industry, some were suitable for food use. Their advantages over natural colourants were:

- (a) Better range of colours.
- (b) High colouring effect/mass ratio.
- (c) Better stability.
- (d) Less batch-to-batch variation.
- (e) Pure and chemically defined.
- (f) Relatively cheap.

Over the past 20–30 years there has been general concern about the safety of food additives as a whole, and especially food colours. Particular concern has been mounting over their relationship to certain allergic responses in children. Gaunt² commented that many of the synthetic colourants selected for use in foods, and the manner in which they are employed, leave much to be desired from a safety viewpoint. Nevertheless, synthetic colourants still remain the most important group of colourants used within the food and drinks industry, though a survey of the patent literature over the past decade indicates quite clearly a trend towards the use of natural colourants. This is partly because of the implication that being natural, they are toxicologically safe.

The trend towards the use of natural ingredients in foodstuffs is continuing and this is evidenced by consumer acceptance of 'natural' foods and the various national regulations which completely or selectively ban artificial ingredients, especially colours, from food. The instability of certain synthetic colourants added to food products is a well-known phenomenon; the products of such instability may import undesirable characteristics to the food and in extreme cases be toxic to the consumer. Many attempts have been made to rationalise the parameters which affect colour stability in foods, but the whole area is so vast that very little has been achieved so far.

The aim of this chapter is to review the common classes of dye used to colour food within the UK and EU. The classes of food colourants reviewed within this chapter include azo, triarylmethane, xanthene, quinoline, indigoid, dicinnamoylmethane, anthraquinone, carotenoid, porphyrin, betalaine, anthocyanin and melanoidin dyes. Scotter³ has extensively reviewed methods of analysis for Riboflavin (E101), Vegetable Carbon (E153), Calcium Carbonate (E170), Titanium Dioxide (E171) and Iron Oxides/Hydroxides (E172).

8.2 UK and EU legislation

As a result of the industrial revolution, in the nineteenth century, pressure was put on the food industry to produce enough food to sustain a rapidly growing population. This resulted in some rather unscrupulous traders exploiting the value of colourings to sell low quality or even spoiled goods. Furthermore during this period, many of the colourings used were toxic therefore putting the consumer at a double risk, e.g. used tea leaves were tinted with black lead and then resold.

In 1820 Frederick Accum revealed some appalling London practices in his book *A Treatise on Adulterations of Food and Culinary Poisons*.⁴ In it he gave names of traders who had been convicted plus an analysis of their wares. This book was the first serious attempt to establish simple reliable analytical tests to determine whether food samples had been adulterated, and was closely followed by a similar work by Hassal⁵ in 1857.

The food analyses by Accum and Hassal, together with public outcry, led to the Adulteration of Foods and Drinks Act of 1860 which was reinforced by the Public Health Act of 1875, as a result of which local authorities were required to appoint public analysts and to institute regular sampling procedures in an attempt to clamp down on food adulteration.

After these initial guidelines and despite the fact that synthetic food colours had been used for some years, the first in-depth consideration of food colour legislation was carried out by a Health Department Committee in 1923. Despite recommendations that, as in the USA, a 'positive' list of colours should be developed (i.e. only colours proven to be non-injurious to health should be permitted in foods), the Government decided in the Public Health Regulations⁶ of 1925 that a list of colours to be prohibited from use due to their toxicity was all that was required. This unfortunately allowed virtually any synthetic colours not on the list to be used in food. However, this Regulation did prohibit the use of harmful colourants including the vegetable colouring matter Gamboge and compounds of antimony, arsenic, cadmium, chromium, copper, lead, mercury and zinc. From 1925, toxicological evidence on many of the colours being used accumulated and eventually,

in 1954, the Food Standards Committee of the Ministry of Food produced a report⁷ favouring a new 'positive' list of colours judged to be harmless, and the abandoning of the 1925 prohibited list concept. In 1957 the Colouring Matters in Food Regulations⁸ followed up this report, allowing some 30 synthetic organic colours. All the recommended colours of natural origin were also included and in addition Indigo, Osage Orange, Safflower, Sandalwood, Titanium Dioxide, Ultramarine and colouring matter natural to edible fruit and vegetables were added to the list; silver and aluminium were permitted for external colouring of certain confectionary. Additionally, the aluminium and calcium lakes of any permitted water-soluble colours were also permitted. This number was reduced to 24 by a 1966 amendment.⁹

On the accession of the UK into the European Economic Community (EEC) new Regulations were introduced to fall in line with the EEC Council Directive of November 1962. This resulted in the delisting of some colours and the listing of others not previously used in the Colouring Matter in Food Regulations (1973). Also, the UK was able to negotiate special temporary provisions for its own traditional colours until 1977, but it was recognised that a move towards full EEC harmonisation was required.

Council Directive 89/107/EEC of 21 December 1989 on the approximation of the laws for the Member States concerning food additives authorised for use in foodstuffs intended for human consumption, the so-called 'Framework Directive' on food additives,¹⁰ contains a list of categories of additives for which further more specific provisions have been drawn up; colours are included in this list. Under criteria specified in the framework additives Directive, food additives may only be approved if they can demonstrate a useful purpose, are safe and do not mislead the consumer.

According to the Colours Directive (European Parliament and Council Directive 94/36/EC of 30 June 1994),¹¹ colours are used to restore the original appearance of food whose colour has been affected by processing, storage, packaging and distribution, as well as to make foods more visually appealing and help identify flavours normally associated with particular foods and to give colours to foods otherwise colourless. Colours are also used to reinforce existing food colour. The Directive contains a list of permitted colours and foods to which they may be added, together with the maximum limits of use. Colours for the purposes of the Directive include substances adding or restoring colour to a food, and natural constituents of foods and natural sources not normally consumed as foods or considered food ingredients. Preparations from natural source material, obtained by physical or chemical extraction, resulting in a selective extraction of nutritive or aromatic constituents, are also colours. However, dried or concentrated foods and flavourings with a secondary colouring effect (e.g. saffron or paprika) and colours used for colouring inedible external parts of foods such as cheese coatings are not considered as colours.

The Directive is divided into five annexes:

Annex I – A list of permitted food colours.

Annex II – A list of foods that may not contain added colours, except where specifically provided for in other annexes.

Annex III – A list of foods for which certain colours only may be added.

Annex IV – A list of colours permitted for certain uses only, e.g. Brown FK, Canthaxanthin, Annatto and Erythrosine.

Annex V – Part 1 contains a list of colours that may be used in accordance with *quantum satis* in foods other than those listed in Annexes II and III (e.g. Carotenes and Beetroot Red); Part 2 contains a list of colours permitted singly or in combination in named foods in accordance with maximum stated limits (e.g. Allura Red, Tartrazine and Cochineal/Carmine).

The term *quantum satis* means that no maximum level is specified. However, colours must be used in accordance to Good Manufacturing Practice at a level not higher than is necessary to achieve the intended purpose.

The UK implemented the provisions of the Colours Directive by means of the Colouring in Food Regulations 1995, SI. 1995 No 3124, as amended.¹² The Regulations contain a list of colours permitted in food and drink products (see Table 8.1) and lists of foods that may or may not be coloured.

The effect of the implementation was to introduce a number of new restrictions on the use of colours, concerning both levels and foods to which colours may be added. Commission Directive 2008/128/EC¹³ has subsequently laid down specific purity criteria for permitted food colours. The Directive prescribes a positive list of approved colours along with limitations on their use. Following a European Food Safety Authority (EFSA) evaluation in 2007¹⁴ of the food colouring Red 2G the use of this dye for colouring food within the EU was banned¹⁵

The UK Food Standards Agency (FSA) has recently called for a voluntary ban of certain artificial colours following the Southampton study¹⁶ on the effect of certain azo dyes (along with benzoate) on children's behaviour. McCann *et al.*'s¹⁶ study concluded that exposure to two mixtures of four synthetic colours plus a sodium benzoate preservative in the diet result in increased hyperactivity in 3-year-old and 8- to 9-year-old children in the general population. The synthetic colours used within the study were Tartrazine, Quinoline Yellow, Sunset Yellow FCF, Ponceau 4R, Allura Red AC and Carmoisine.

Table 8.1 Permitted food colours according to the Colouring in Food Regulations 1995, SI. 1995 No 3124, as amended¹²

Colour	EC No.	Class	Einecs
Curcumin	E100	Dicinnamoylmethane	207–280–5
(i) Riboflavin	E101	Isoalloxazine	201–507–1
(ii) Riboflavin-5'-Phosphate			204–988–6
Tartrazine	E102	Monoazo	217–699–5
Quinoline Yellow	E104	Chinophthalone	305–897–5
Sunset Yellow FCF (Orange Yellow S)	E110	Monoazo	220–491–7
Cochineal	E120	Anthraquinone	215–680–6
Carminic acid			215–023–3
Carmines			215–724–4
Azorubine, Carmoisine	E122	Monoazo	222–657–4
Amaranth	E123	Monoazo	213–022–2
Ponceau 4R, Cochineal Red A	E124	Monoazo	220–036–2
Erythrosine	E127	Xanthene	240–474–8
Allura Red AC	E129	Monoazo	247–368–0
Patent Blue V	E131	Triarylmethane	222–573–8
Indigotine, Indigo Carmine	E132	Indigoid	212–728–8
Brilliant Blue FCF	E133	Triarylmethane	223–669–8
Chlorophylls	E140	Porphyrin	215–800–7
Chlorophyllins			287–483–3
Copper complexes of Chlorophylls and Chlorophyllins	E141	Porphyrin	Cu chlorophyll a 239–830–5 Co chlorophyll b 246–020–5
Green S	E142	Triarylmethane	221–409–2
Plain Caramel†	E150a	Melanoidin	232–435–9
Caustic Sulphite Caramel	E150b	Melanoidin	232–435–9
Ammonia Caramel	E150c	Melanoidin	232–435–9
Sulphite ammonia Caramel	E150d	Melanoidin	232–435–9
Brilliant Black BN, Black PN	E151	Diazo	219–746–5
Vegetable Carbon	E153	–	215–606–9
Brown FK	E154	Azo (a mixture of mono-, di- and triazo colours)	–
Brown HT	E155	Diazo	224–924–0
Carotenes	E160a	Carotenoid	230–636–6
(i) Mixed carotenes			
(ii) Beta-carotene			
Annatto	E160b	Carotenoid	215–735–4
Bixin			289–561–2
Norbixin			230–248–7

(Continued)

Table 8.1 Continued

Colour	EC No.	Class	Einecs
Paprika extract, Capsanthin, Capsorubin	E160c	Carotenoid	Capsanthin 207–364–1 Capsorubin 207–425–2
Lycopene	E160d	Carotenoid	–
Beta-apo-8'-carotenal	E160e	Carotenoid	214–171–6
Ethyl ester of beta-apo-8'-carotenal	E160f	Carotenoid	214–173–7
Lutein	E161b	Carotenoid	204–840–0
Canthaxanthin	E161g	Carotenoid	208–187–2
Beetroot Red, betanin	E162	Betalaine	231–628–5
Anthocyanins	E163	Anthocyanin	Cyanidin 208–438–6 Peonidin 205–125–6 Delphinidin 208–437–0 Malvidin 211–403–8 Pelargonidin 205–127–7
Calcium Carbonate	E170	Inorganic	207–439–9
Titanium Dioxide	E171	Inorganic	236–675–5
Iron Oxides and Hydroxides	E172	Inorganic	Fe oxide yellow 257–098–5 Fe oxide red 215–168–2 Iron oxide black 235–442–5
Aluminium	E173	Inorganic	231–072–3
Silver	E174	Inorganic	231–131–3
Gold	E175	Inorganic	231–165–9
Litholrubine BK	E180	Monoazo	226–109–5

† The term caramel relates to products of a more or less intense brown colour that are intended for colouring. It does not correspond to the sugary aromatic product obtained from heating sugars and which is used for flavouring food (e.g. confectionery, pastry and alcoholic drinks).

Further work undertaken by the EFSA Panel on Food Additives, Flavourings, Processing Aids and Food Contact Materials¹⁷ concluded that McCann *et al.*'s study¹⁶ provided limited evidence that the two different mixtures of synthetic colours and sodium benzoate tested had a small and statistically significant effect on activity and attention in children selected from the general population excluding children medicated for attention deficit hyperactivity disorder (ADHD), although the effects were not statistically significant for the two mixtures in both age groups. Since mixtures and

not individual additives were tested in the study by McCann *et al.*, EFSA commented that it was not possible to ascribe the observed effects to any of the individual compounds and the clinical significance of the observed effects also remains unclear. In the context of the overall weight of evidence and in view of the considerable uncertainties, such as the lack of consistency and relative weakness of the effect and the absence of information on the clinical significance of the behavioural changes observed, the Panel concluded that the findings of the study cannot be used as a basis for altering the acceptable daily intake (ADI) of the respective food colours or sodium benzoate.

Following a request from the European Commission, the EFSA Panel on Dietetic Products, Nutrition and Allergies was asked to provide a scientific opinion,¹⁸ in the light of the most recent scientific evidence, on the appropriateness of the food azo colours Tartrazine, Sunset Yellow FCF, Carmoisine, Amaranth, Ponceau 4R, Allura Red AC, Brilliant Black BN, Brown FK, Brown HT and Litholrubine BK for inclusion in the list of food ingredients set up in Annex IIIa of Directive 2000/13/EC,¹⁹ as amended. The Panel concluded that it is unlikely that oral consumption of the food colours under consideration, either individually or in combination, would trigger severe adverse reactions in human subjects at the current levels of use.

8.3 Synthetic food colours

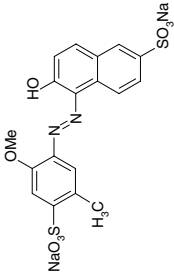
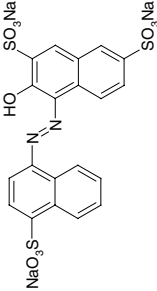
8.3.1 Azo dyes

The azo dyes currently permitted for use within the EU are Tartrazine, Sunset Yellow FCF, Carmoisine, Amaranth, Ponceau 4R, Allura Red AC, Brown FK, Brown HT, Brilliant Black BN and Litholrubine BK (Table 8.2).

Coulson⁴⁴ reported that azo dyes are manufactured by reacting (coupling) a diazotised primary aromatic amine (diazo component) with a coupling component (usually an aromatic amine, hydroxyl compound or keto compound capable of enolisation) in an electrophilic aromatic substitution reaction. The di, tri and poly azo dyes are manufactured by either using a diamine or polyfunctional coupling component as starting material or by repeating the process with an aminoazo compound. As diazonium ions are relatively weak electrophilic reagents, the aromatic coupling components must carry a powerful electron donor group (e.g. $-\text{OH}$ or $-\text{NH}_2$). In an acidic medium the aromatic amine is converted into a diazonium at *ca.* 5°C by the addition of sodium nitrite.

These are the most commonly used synthetic dyes where the chromophoric system consists of the azo group in association with one or more aromatic systems. Many of the colours termed 'azo' do not possess a true azo

Table 8.2 Azo food colours permitted for use within the EU

Synthetic dye	Structure
<p>Allura Red (E129)</p> <p><i>Synonyms</i> – FD&C Red No. 40, C.I. 16035</p> <p><i>Chemical name</i> – Disodium 2-hydroxy-1-(2-methoxy-5-methyl-4-sulphonatophenylazo)naphthalene-6-disulphonate</p> <p><i>Empirical formula</i> – $C_{18}H_{14}N_2Na_2O_8S_2$</p> <p><i>Molecular weight</i> – 496.42</p> <p>Acceptable daily intake</p> <p>SCF – 7 mg/kg bodyweight/day²⁰</p> <p>JECFA – 7 mg/kg bodyweight/day²¹</p> <p>EFSA – 7 mg/kg bodyweight/day²²</p>	
<p>Amaranth (E123)</p> <p><i>Synonyms</i> – C.I. 16185</p> <p><i>Chemical name</i> – Trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo)naphthalene-3,6-disulphonate</p> <p><i>Empirical formula</i> – $C_{20}H_{11}N_2Na_3O_{10}S_3$</p> <p><i>Molecular weight</i> 604.48</p> <p>Acceptable daily intake</p> <p>SCF – 0.8 mg/kg bodyweight/day²³</p> <p>JECFA – 0.5 mg/kg bodyweight/day²⁴</p> <p>EFSA – 0.15 mg/kg bodyweight/day²⁵</p>	

Brown FK (E154)

Synonyms – C.I. Food Brown 1

Chemical name

A mixture of:

I Sodium 4-(2,4-diaminophenylazo)benzenesulphonate

II Sodium 4-(4,6-diamino-m-tolylazo)benzenesulphonate

III Disodium 4,4'-(4,6-diamino-1,3-phenylenebisazo)di(benzenesulphonate)

IV Disodium 4,4'-(2,4-diamino-1,3-phenylenebisazo)di(benzenesulphonate)

V Disodium 4,4'-(2,4-diamino-5-methyl-1,3-phenylenebisazo)di(benzenesulphonate)

VI Trisodium 4,4',4''-(2,4-diaminobenzene-1,3,5-trisazo)tri(benzenesulphonate)

Empirical formulae

I $C_{12}H_{11}N_4NaO_3S$

II $C_{13}H_{13}N_4NaO_3S$

III $C_{18}H_{14}N_6Na_2O_6S_2$

IV $C_{18}H_{14}N_6Na_2O_6S_2$

V $C_{19}H_{16}N_6Na_2O_6S_2$

VI $C_{24}H_{17}N_8Na_3O_9S_3$

Molecular weights

I 314.30

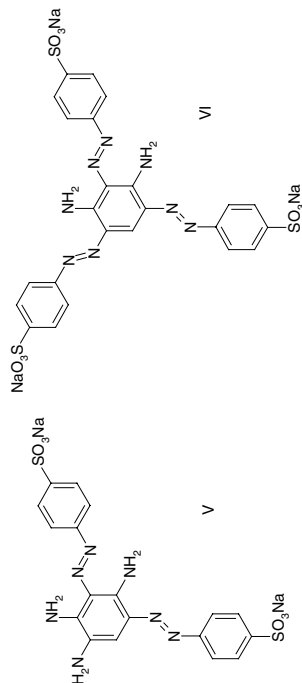
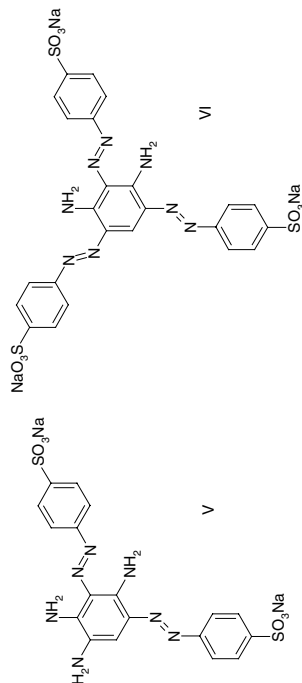
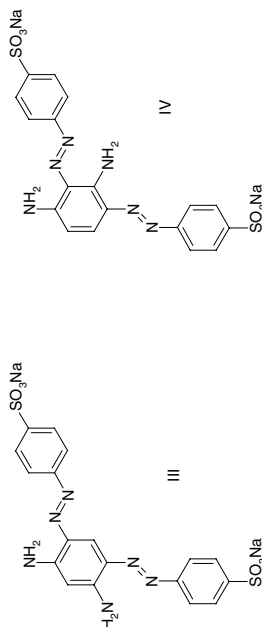
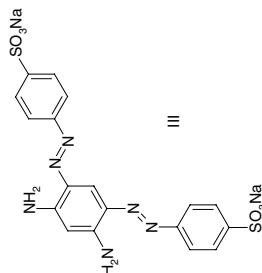
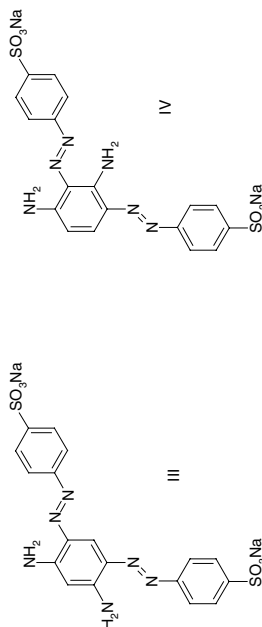
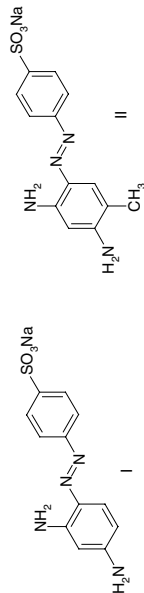
II 328.33

III 520.46

IV 520.46

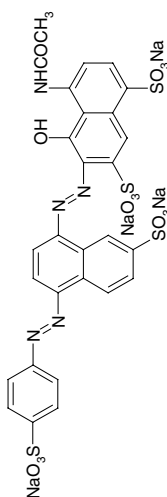
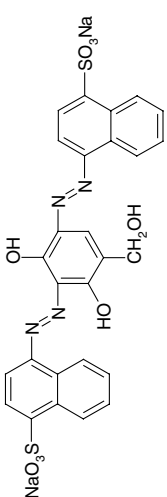
V 534.47

VI 726.59



(Continued)

Table 8.2 Continued

Synthetic dye	Structure
<p><i>Acceptable daily intake</i> SCF – 0.15 mg/kg bodyweight/day²⁶ JECFA – No ADI EFSA – Unable to conclude on the safety of Brown FK given the deficiencies in the available toxicity database on the colour.</p>	
<p>Brilliant Black BN (E151) <i>Synonyms</i> – C.i. 28440 (Food black 1) <i>Chemical name</i> – Tetrasodium 4-acetamido-5-hydroxy-6-[7-sulphonato-4-(4-sulphonatophenylazo)-1-naphthylazo]naphthalene-1,7-disulphonate <i>Empirical formula</i> – $C_{28}H_{17}N_5Na_4O_{14}S_4$ <i>Molecular weight</i> – 867.69 <i>Acceptable daily intake</i> SCF – 5 mg/kg bodyweight/day²⁷ JECFA – 1 mg/kg bodyweight/day²⁸ EFSA – 5 mg/kg bodyweight/day²⁹</p>	
<p>Brown HT (E155) <i>Synonyms</i> – C.i. 20285 (Food Brown 3), Chocolate Brown HT <i>Chemical name</i> – Disodium 4,4'-(2,4-dihydroxy-5-hydroxymethyl-1,3-phenylenebisazo)di(naphthalene-1-sulphonate) <i>Empirical formula</i> – $C_{27}H_{18}N_4Na_2O_9S_2$ <i>Molecular weight</i> – 652.57 <i>Acceptable daily intake</i> SCF – 3 mg/kg bodyweight/day²⁶ JECFA – 1.5 mg/kg bodyweight/day³⁰ EFSA – 1.5 mg/kg bodyweight/day³¹</p>	

Carmoisine (E122)

Synonyms – C.I. 14720 (Food Red 3), azorubine

Chemical name – Disodium 4-hydroxy-3-(4-sulphonato-1-naphthylazo)naphthalene-1-sulphonate

Empirical formula – $C_{20}H_{12}N_2Na_2O_7S_2$

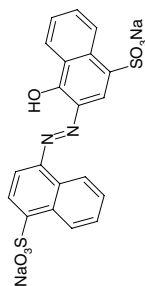
Molecular weight – 502.44

Acceptable daily intake

SCF – 4 mg/kg bodyweight/day³²

JECFA – 4 mg/kg bodyweight/day³³

EFSA – 4 mg/kg bodyweight/day³⁴



Ponceau 4R (E124)

Synonyms – C.I. 16255 (Food Red 7), Cochineal Red A, Food Red 102

Chemical name – Trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo)naphthalene-6,8-disulphonate

Empirical formula – $C_{20}H_{11}N_2Na_3O_{10}S_3$

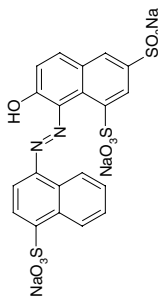
Molecular weight – 604.48

Acceptable daily intake

SCF – 4 mg/kg bodyweight/day²⁷

JECFA – 4 mg/kg bodyweight/day³⁵

EFSA – 0.7 mg/kg bodyweight/day³⁶



Sunset Yellow FCF (E110)

Synonyms – C.I. 15985 (Food Yellow 3), FD&C Yellow No.6, Orange

Yellow S

Chemical name – Disodium 2-hydroxy-1-(4-sulphonatophenylazo)naphthalene-6-sulphonate

Empirical formula – $C_{16}H_{10}N_2Na_2O_7S_2$

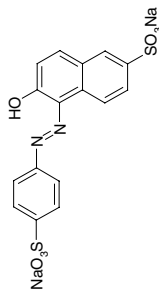
Molecular weight – 452.37

Acceptable daily intake

SCF – 2.5 mg/kg bodyweight/day²⁷

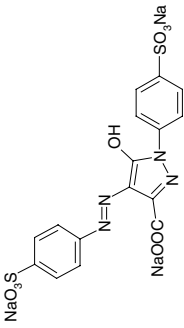
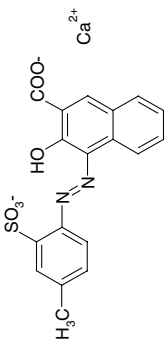
JECFA – 2.5 mg/kg bodyweight/day³⁷

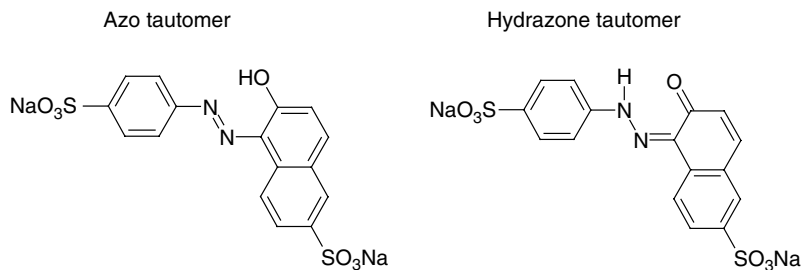
EFSA – 1 mg/kg bodyweight/day³⁸



(Continued)

Table 8.2 Continued

Synthetic dye	Structure
<p>Tartrazine (E102)</p> <p>Synonyms – C.I. 19140 (Food Yellow 4), FD&C Yellow No.5</p> <p>Chemical Name – Trisodium 5-hydroxy-1-(4-sulphonatophenyl)-4-(4-sulphonatophenylazo)-H-pyrazole-3-carboxylate</p> <p>Empirical formula – $C_{16}H_9N_4Na_3O_9S_2$</p> <p>Molecular weight – 534.37</p> <p>Acceptable daily intake</p> <p>SCF – 75 mg/kg bodyweight/day²⁷</p> <p>JECFA – 7.5 mg/kg bodyweight/day³⁹</p> <p>EFSA – 7.5 mg/kg bodyweight/day⁴⁰</p>	
<p>Litholrubine BK (E180)</p> <p>Synonyms – C.I. 15850:1 (Pigment Red 57.1), D&C Red No. 7</p> <p>Chemical name – Calcium 3-hydroxy-4-(4-methyl-2-sulphonatophenylazo)-2-naphthalenecarboxylate</p> <p>Empirical formula – $C_{18}H_{12}CaN_2O_6S$</p> <p>Molecular weight – 424.45</p> <p>Acceptable daily intake</p> <p>SCF – 1.5 mg/kg bodyweight/day⁴¹</p> <p>JECFA – No ADI⁴²</p> <p>EFSA – No ADI⁴³</p>	



8.1 Azo-hydrazone tautomerism.

linkage but exist rather as an azo-hydrazone tautomer, e.g. Sunset Yellow FCF (Fig. 8.1).

Azo-hydrazone tautomerism arises when hydroxyl groups are present *ortho* or *para* to the azo group. In almost all cases (hydroxyphenyl derivatives being the exception) the dominant form under application conditions is the hydrazone tautomer.⁴⁵ The actual stability of azo-hydrazone tautomers differs markedly between the two and has been well documented.

8.3.2 Triarylmethane dyes

Triarylmethane colours (Table 8.3) are distinguished by their brilliance of colour and high tinctorial strength, but they have poor light-fastness properties. The chromophoric system consists of a central carbon atom joined to three aromatic rings generally with hydroxyl, amino and substituted amino substitutes in the *para*-position acting as auxochromes.

Coulson⁴⁴ reported the synthesis of triarylmethane dyes to proceed stepwise from mono- via di- and triarylcarbonium compounds. Materials containing a central carbon atom as the electrophilic reaction centre are reacted with an aromatic nucleophile. This reaction can be repeated up to three times provided the central carbon atom is electrophilic. Green S is produced by initially condensing bis-dimethylaminobenzhydrol with 2-hydroxynaphthalene-3,6-disulphonic acid in the presence of concentrated sulphuric acid with the elimination of water to give a leuco-base. Oxidation with manganese dioxide in weakly acidic conditions yields Green S.

8.3.3 Xanthene dyes

In the xanthene group of colours the chromophoric system is the xanthene or dibenzo-1,4-pyran heterocyclic ring system with amino or hydroxyl groups in the *meta* position with respect to the oxygen bridge. Generally, a further aromatic ring is attached to the xanthene system analogous to the

Table 8.3 Triarylmethane food colours permitted for use within the EU

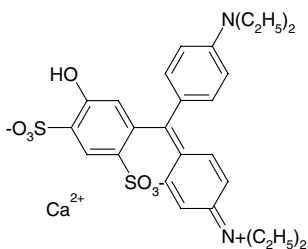
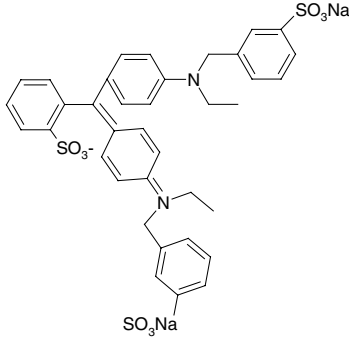
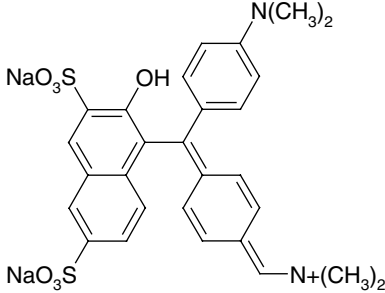
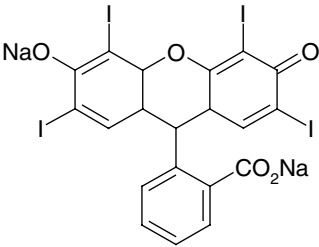
Synthetic dye	Structure
<p>Patent Blue V (E131) Synonym – C.I. 42051 (Food Blue 5) Chemical name – The calcium or sodium compound of [4-(α-(4-diethylaminophenyl)-5-hydroxy-2,4-disulphophenyl-methylidene)-2,5-cyclohexadien-1-ylidene] diethylammonium hydroxide inner salt Empirical formulae – Calcium compound: $C_{27}H_{31}N_2O_7S_2Ca^{2+}$; Sodium compound: $C_{27}H_{31}N_2O_7S_2Na$ Molecular weights – Calcium compound: 579.72; Sodium compound: 582.67 Acceptable daily intake SCF – 15 mg/kg bodyweight/day JECFA – No ADI set EFSA – No ADI set</p>	
<p>Brilliant Blue FCF (E133) Synonyms – C.I. 42090 (Food Blue 2), FD&C Blue No.1 Chemical name – Disodium α-(4-(N-ethyl-3-sulphonatobenzylamino)phenyl)-α-(4-N-ethyl-3-sulphonatobenzylamino) cyclohexa-2,5-dienylidene) toluene-2-sulphonate Empirical formula – $C_{37}H_{34}N_2Na_2O_9S_3$ Molecular weight – 792.84 Acceptable daily intake SCF – 10.0 mg/kg bodyweight/day²⁷ JECFA – 12.5 mg/kg bodyweight/day⁴⁶ EFSA – 6 mg/kg bodyweight/day⁴⁷</p>	
<p>Green S (E142) Synonyms – C.I. 44090 (Food Green 4), Brilliant Green BS Chemical name – Sodium 5-[4-dimethylamino-α-(4-dimethyliminocyclohexa-2,5-dienylidene)benzyl]-6-hydroxy-7-sulphonato-naphthalene-2-sulphonate Empirical formula – $C_{27}H_{25}N_2Na_2O_7S_2$ Molecular weight – 576.63 Acceptable daily intake SCF – 5 mg/kg bodyweight/day²⁷ JECFA – No ADI EFSA – No ADI</p>	

Table 8.4 Xanthene food colours permitted for use within the EU

Synthetic dye	Structure
<p>Erythrosine (E127)</p> <p><i>Synonyms</i> – C.I. 45430 (Food Red 14), FD&C Red 3</p> <p><i>Chemical name</i> – Disodium 2-(2,4,5,7-tetraiodo-3-oxido-6-oxoxanthen-9-yl)benzoate monohydrate</p> <p><i>Empirical formula</i> – $C_{20}H_6I_4Na_2O_5 \cdot H_2O$</p> <p><i>Molecular weight</i> – 897.88</p> <p><i>Acceptable daily intake</i></p> <p>SCF – 0.1 mg/kg bodyweight/day</p> <p>JECFA – 0.1 mg/kg bodyweight/day</p> <p>EFSA – No ADI</p>	

triarylmethane dyes. Erythrosine is the only xanthene dye permitted in the EU or the USA for colouring food (Table 8.4).

Erythrosine is usually manufactured by the condensation of resorcinol with phthalic anhydride by fusion in the presence of concentrated sulphuric acid or zinc chloride, with the elimination of two molecules of water yield Fluorescein (C.I. 45350).⁴⁴ Treatment of a boiling alcoholic solution of Fluorescein with iodine and potassium iodate produces Erythrosine.⁴⁸

8.3.4 Quinoline dyes

In quinoline dyes the chromophoric system is the quinophthalone or 2-(2-quinoly)-1,3-indandione heterocyclic ring system. In addition, the quinoline dyes invariably contain a small amount of the isomeric phthalyl derivatives. Quinoline Yellow is the only dye in this group of importance for use in food colouration (Table 8.5).

Quinoline Yellow is typically manufactured by condensation of quinaldine (2-methylquinoline) with phthalic anhydride by fusion at *ca.* 220°C in the presence of zinc chloride, and sulphonation of the product with oleum at around 90°C.⁴⁴ Sulphonation occurs in the quinoline ring and the disulphonated product predominates.⁴⁸

8.3.5 Indigoid dyes

The indigoid group of food colours is based on synthetic equivalents of naturally occurring Indigo (C.I. 75780). Colour is due to a resonance hybrid of structures or a tetrapole structure.

In their crystalline state, at least, they are normally in the *trans* configuration. The only food colour of importance in this group is Indigo Carmine (Table 8.6).

Table 8.5 Quinoline food colours permitted for use within the EU

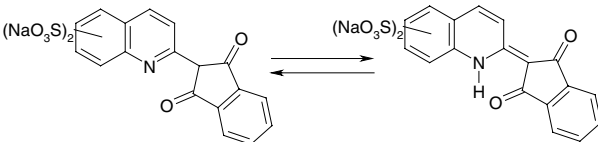
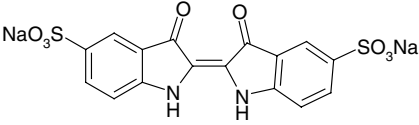
Synthetic dye	Structure
<p>Quinoline Yellow (E104)</p> <p><i>Synonym</i> – C.I. 47005 (Food Yellow 13)</p> <p><i>Chemical name</i> – The disodium salts of the disulphonates of 2-(2-quinolyl) indan-1,3-dione (principal component)</p> <p><i>Empirical formula</i> $C_{18}H_9NNa_2O_8S_2$ (principal component)</p> <p><i>Molecular weight</i> – 477.38 (principal component)</p> <p><i>Acceptable daily intake</i> SCF – 10 mg/kg bodyweight/day⁴⁹ JECFA – 10 mg/kg bodyweight/day⁵⁰ EFSA – 0.5 mg/kg bodyweight/day⁵¹</p>	

Table 8.6 Indigoid food colours permitted for use within the EU

Synthetic dye	Structure
<p>Indigo carmine (E132)</p> <p><i>Synonyms</i> – C.I. 73015 (Food Blue 1), FD&C Blue No. 2</p> <p><i>Chemical name</i> – Disodium 3,3'-dioxo-2,2'-bi-indolylidene-5,5'-disulphonate</p> <p><i>Empirical formula</i> – $C_{16}H_8N_2Na_2O_8S_2$</p> <p><i>Molecular weight</i> – 466.36</p> <p><i>Acceptable daily intake</i> SCF – 5 mg/kg bodyweight/day JECFA – 5 mg/kg bodyweight/day EFSA – No ADI</p>	

Indigo carmine is typically produced from indigo (C.I. 73000).⁴⁴ Indigo is sulphonated with concentrated sulphuric acid at *ca.* 90°C. Indigo carmine is the 5,5'-disulphonated reaction product and is isolated as the sodium salt.

8.3.6 Synthetic dye purity

Commission Directive 2008/128¹³ lays down specific purity criteria for colours used in foodstuffs. The purity of synthetic food dyes is generally better than 80% with the remainder consisting of subsidiary dyes, starting materials, intermediates or other contaminants.

Inorganic impurities

The amount of insoluble matter in a dye is an indication of its purity. In addition, insoluble matter causes practical problems for the user, such as cloudy drinks, gritty toothpaste, blocked plant filters, etc. Inorganic salts present in a food colour are there as a result of a step in the manufacturing procedure, for example neutralisation, isolation, iodination, etc., or because of a deliberate action by the manufacturer to meet the strength requirement of the consumer. The most common salts found are sodium sulphate and sodium chloride. There are also small amounts of sodium acetate, sodium phosphate, sodium iodate and sodium carbonate. Trace metals are present in azo food dyes owing to the equipment used and impurities in the raw materials.

Organic impurities

There are several kinds of organic impurity that may be present in an azo food dye. These include impurities already present in the raw materials, isomeric colourants, subsidiary colourants, decomposition compounds, compounds formed from side reactions, and chance contaminants.

The most common impurities expected are small amounts of the 'intermediates' used in the synthesis of food dyes. Many of these are sulphonated as a result of the sulphonation step in dye manufacture. The purity of the starting materials is also very important.⁵² As an example consider 2-naphthol-6-sulphonic acid, which is used in the preparation of Sunset Yellow. It is produced by sulphonating naphthalene, fusing a salt of the resulting sulphonic acid with alkali to form 2-naphthol, sulphonating it, then converting the compound to 2-naphthol-6-sulphonic acid. In principle the final compound should be 2-naphthol-6-sulphonic acid, but Marmion⁵² showed that a variety of compounds may also be formed. The fate of these impurities depends on their structure.

Those that can couple, such as 2-naphthol, 2-naphthol-3,6-disulphonic acid, G-salt and Crocein acid, can either persist in the finished colourant unchanged, or can react to form isomeric and subsidiary dyes.⁵² Lancaster and Lawrence⁵³ showed that the most frequently found subsidiary colours in Amaranth, Sunset Yellow and Tartrazine are higher and lower sulphonated

subsidiary dyes. Those that cannot couple like naphthalene-di and trisulphonic acids and 6,6'-oxybis(2-naphthalenesulphonic acid) (DONS) often are carried over into the finished product. Also difficult to predict is the presence of impurities which arise as a result of certain side reactions, for example 4,4'-diazaminobis(5-methoxy-2-methylbenzenesulphonic acid) (DMMA) often found in Allura Red, and 4,4'-(diazamino)-dibzenesulphonic acid (DAADBSA) frequently found in Sunset Yellow. Both are a result of using insufficient amounts of nitrite or acid during the manufacture of the colourants. DMMA is produced when cresidine diazosulphonic acid (CSA) combines with undiazotised CSA.

As well as the sulphonated impurities, there may well also be various unsulphonated compounds which are present owing to impurities in the starting materials. Technical grade 4-aminophenyl-1-sulphonic acid typically contains 0.1–0.2% aniline⁵⁴ and other unsulphonated amines may be present as a consequence of the aniline contamination. For example, benzidine levels of 5–50ppm have been found in technical grade 4-aminophenyl-1-sulphonic acid.⁵⁵ Reaction between diazotised and undiazotised aniline forms 1,3-diphenyltriazene, which can rearrange to form 4-aminoazobenzene (4-AAB).⁵⁶ Thermal⁵⁷ or photochemical⁵⁸ decomposition of 1,3-diphenyl triazene can lead to formation of 4-aminobiphenyl, all of which have been found in Sunset Yellow.⁵⁹

8.3.7 Stability of synthetic food colours

In general the permitted synthetic food colours are stable for most uses in food. In the dry state no degradation has been noted, other than loss of dye strength due to moisture absorption.⁶⁰ In food media azo dyes undergo fading to various degrees upon heating and storage to give rise to colourless and coloured subsidiary compounds.

The stability of synthetic food colours towards the conditions prevailing in food processing depends upon a number of factors. These include the media in which the colour is used, the colourant concentration and concentration of other additives, and the temperature and time of exposure. Changes that occur as a result of these factors vary for each colour used so that all the components of the blend of food colours will not fade at the same rate.

Effect of food processing temperatures and storage

An extensive investigation of the changes occurring to permitted food colourants on processing and storage was carried out in 1963.⁶¹ The stability of individual colours has also been investigated.^{62,63} This work showed that the dyes of the FD&C Red No. 2 series (Amaranth) were all less stable than the respective dyes of the FD&C Yellow No. 6 (Sunset Yellow) series. It also

reported that the addition of two sulphonic acid groups to the 6,8 positions versus the 3,6 positions of the 2-naphthol ring resulted in decreased stability. These include Carmoisine, Sunset Yellow, Erythrosine and Indigo Carmine.

Temperatures used in cooking can be detrimental to food colour stability. The most stable of the commonly used synthetic colours to high temperatures are Ponceau 4R, Allura Red, Sunset Yellow, Tartrazine, Chocolate Brown HT, Green S and Brilliant Blue.^{62–65} Brownley and Lachman⁶⁵ reported that Indigo Carmine is not stable to high temperatures. At very high temperatures some carbonisation may occur which will cause colour loss and change of shade.

Nursten and Williams⁶⁶ showed that Amaranth readily desulphonates when in the free acid form, on heating at 100°C.

Action of light

The general photochemistry of azo and hydrazone dyes has been reviewed in detail.⁶⁷ When illuminated, true azo dyes can undergo three principal types of photochemical reaction,⁶⁷ namely *cis-trans* photo-isomerism, photo-reduction and photo-oxidation. The first is of a practical concern, even though it does not result in irreversible destruction of the dye.

Azo dyes exist under normal conditions exclusively in the *trans* form, and light absorption may result in some conversion to the less stable *cis*-isomer. The consequent deepening of colour is reversed on removing the light source. Hydrazone dyes are non-photochromic as the hydroxyl group helps to accelerate *cis-trans* reversion via intra- and inter-molecular hydrogen bonding.

Photo-reduction of azo dyes has been demonstrated to occur primarily by indirect photo-reduction, in which the azo dye itself does not necessarily absorb the active radiation. Van Beck and co-workers⁶⁸ discovered that mandelic acid, in conjunction with ultraviolet (UV) light, is a very active agent in the photo-fading of azo dyes. Photo-oxidative degradation appears to be a much more common phenomenon and occurs on all substrates other than proteins.⁶⁹

Gregory⁷⁰ postulated that singlet oxygen, arising from dye sensitisation of ground state triplet oxygen reacts with the hydrazine tautomers in a thermally allowed 6π process, the Ene reaction, to give a peroxide which would then be expected to decompose to naphthoquinones.

It has been shown that a highly conjugated azo dye system lacks stability to light. The Amaranth molecule contains one more sulphonic acid group and one more additional aromatic ring to the corresponding molecule of Sunset Yellow, hence on the basis of aromaticity, it could be anticipated that Amaranth would be more light sensitive than the latter dye. Tartrazine is more stable, since the pyrazolone portion of the molecule is not truly

aromatic and lacks the pi-electron mobility. Saxby and Reid⁷¹ irradiated Amaranth, Sunset Yellow and Tartrazine with UV light and in the presence of aqueous sulphur dioxide, and found the order of degradation to be:

Amaranth > Sunset Yellow > Tartrazine

Strong sunlight and particularly UV light are capable of bringing about photochemical changes in food colourants resulting in decolourisation.^{72,73} Van Beck *et al.*⁷² showed that irradiation of solutions of azo dyes and other organic compounds with UV radiation under anaerobic conditions result in the photo-reduction of the dyes to the corresponding amines.

Reactions with other food additives

The chemical interactions between food additives have been extensively reviewed by Scotter and Castle.⁷⁴

Action of alkalis and acids

The stability of food colourants to alkalis and acids varies considerably, the azo food dyes showing the best resistance to degradation.

This was tested by investigating the combined effect of heat and pH on dye samples which had been processed in neutral and acidic conditions.^{62,63} Fading of all colours in acidic or alkaline media is accelerated by contact with metals at high temperatures.⁶⁴ Marmion⁵² has extensively reviewed the effect of pH, acids and alkalis on the stability of some colourants. Desai and Giles⁷⁵ showed that the dye Orange II (related to Sunset Yellow) cleaved under acidic conditions in the presence of O₂ to yield a compound thought to be a quinone.

Action of reducing and oxidising agents

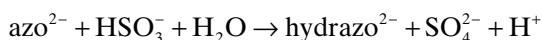
The two main areas in which the majority of permitted food colours show instability are in combination with oxidising and reducing agents. Since many synthetic food colours contain unsaturated bonds they are susceptible to reduction by reducing substances like hydrogen, sugars, acids and salts. The azo and triarylmethane dyes are easily reduced to colourless compounds.⁶⁴

Effect of preservatives

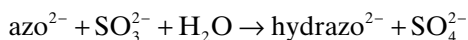
The effect of volatile sulphur compounds liberated from fish proteins during heating processes on colourants was demonstrated by Raven.⁷⁶ Banerjee *et al.*⁷⁷ investigated the interaction of colourants, preservatives and other chemicals in canned foods. It was found that in canned products containing

added colour with tartaric and citric acid, etc., these acted on the tin of the container to liberate hydrogen. This in turn reacts with the dye and reduces it to a colourless compound. It was assumed that Sn^{2+} , a strong reducing agent, was formed by the action of oxygen and nitrate present was reduced to nitrite. Nitrite caused very rapid de-tinning so Sn^{2+} reduces the dye, resulting in a loss of colour.

Wedzicha and Rumbelow⁷⁸ carried out an investigation of the kinetics and mechanisms of the interaction between sulphite species and Carmoisine between pH 4.0 and 5.3. Stoichiometric data and radiochemical analysis of reaction compounds indicated that two electrons are transferred in the reduction of the azo compound with two reactions possibly occurring:



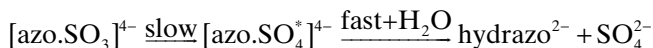
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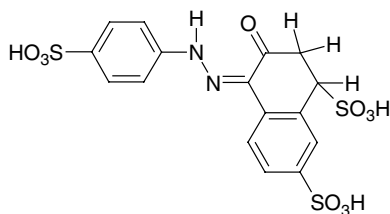
The reaction was found to be first order with respect to azo and sulphite species and showed an order of -1.0 with respect to the hydrogen ion.

$$\frac{d[\text{azo}]}{dt} = \frac{d[\text{HSO}_3^-]}{dt} = \frac{k[\text{HSO}_3^-][\text{azo}^{2-}]}{[\text{H}^+]}$$

The kinetics of the reaction suggested that one molecule of sulphite species and one molecule of the azo compound form a reaction complex and it was suggested that the hydrazo compound was formed via the hydrolysis of the activated complex.



Saxby and Stephen⁷⁹ reported that Sunset Yellow in the presence of SO_2 forms a secondary dye. Substitution of position 4 was found to be a facile process which could be explained by the following mechanism.⁸⁰ The Sunset Yellow molecule is protonated in an acidic medium, which is then subjected to nucleophilic attack by an unionised sulphurous acid molecule. Aromatisation of the quinoid structure occurs by the loss of two hydrogen atoms, a process which could readily take place in the presence of air. Size-exclusion chromatography indicated that this compound formed a dimer which was thought to be the secondary dye.



8.2 Sunset Yellow degradation substance proposed by Damant *et al.*⁸¹ (reproduced with permission of the authors).

Subsequent research undertaken by Damant, Reynolds and Macrae⁸¹ showed that in model samples containing both Sunset Yellow and sodium metabisulphite, the formation of a lemon-yellow-coloured substance was clearly demonstrated. The substance was identified using nuclear magnetic resonance (NMR) and FAB-mass spectrometry (MS) and showed the structure of the lemon-yellow substance to be that resulting from sulphonation at carbon 4 of the sunset yellow molecule (Fig. 8.2).

Ascorbic acid

Colour fading of permitted colourants in carbonated and still soft drinks has been found to be due to ascorbic acid incorporated as an antioxidant and as a vitamin supplement.⁸² Fogg and Summan^{83–86} demonstrated the formation of aniline, 4-aminophenyl-1-sulphonic acid and 4-aminonaphthalene-1-sulphonic acid during degradation of azo dyes under accelerated conditions. These amines were shown to degrade further to ammonia. In particular, 4-aminonaphthalene-1-sulphonic acid was found to degrade rapidly in this way, even in the absence of ascorbic acid, although its degradation was even more rapid in its presence. Azo dyes permitted in the UK were found to be less stable in the presence of ascorbic acid at pH 7.0 and very resistant to change at pH 3.0.⁶⁶

Metals

Contact with metals such as zinc, tin, aluminium and copper was formerly a major factor in dye degradation, especially in canned foods. In canned rhubarb the disappearance of Ponceau 4R was associated with electrochemical reduction of the azo linkage which resulted in splitting of the molecule with the production of two amines.⁷⁶

Sinha and Saker⁸⁷ investigated the interactions of Amaranth with metal ions and found that of the divalent metal ions considered, copper showed considerable interactions by depressing the principal absorption band of the dye between 480 nm and 560 nm with concomitant development of an isobetic point at 473 nm. The ratio of the dye and copper was found to be

1:2 with a pH stability 4.5–8.0 but beyond this range they found the complex dissociated resulting in pure Amaranth and copper. Frazier and Bernhard⁸⁸ could not confirm the formation of a 1:2 complex. They examined the interaction of Sunset Yellow with copper and found that the dye combined with the cupric ion, resulting in a shift in the visible spectrum and in hydrogen being liberated.

Banerjee *et al.*⁸⁹ found that only Amaranth, Ponceau 4R and Sunset Yellow formed complexes with the cupric ion. This was explained by the fact that all these molecules have an *o*-hydroxy group. Other transition metals, e.g. Ni^{2+} , Co^{3+} , Fe^{3+} , Zn^{2+} , etc., have no complexing effect, hence indicating weak donor properties of these dyes. Banerjee *et al.* presented arguments for their conclusions by saying that dyes reacted with cupric ion in ratios of 1:1 and 1:2 dye. They proposed that at pH 4.5 the *o*-hydroxyazo hydrogen is replaced. The reaction, because it involves the chromophore of the molecule, would produce a spectral shift, and such a shift was observed. They proposed that at pH 6.0 the cupric ion neutralises the two sulphonic acid groups via a 'salt forming equilibrium' with the exact location of the second cupric ion being unknown. The 1:1 complex presented associates the cupric ion with the α -nitrogen. The interaction between the azo group and cupric ion should be with the β -nitrogen.^{56,90,91} The β -nitrogen is slightly more electronegative than the α -nitrogen because the oxygen *ortho* to the α -nitrogen tends to draw electrons from the α -nitrogen. Also the six membered ring formed by the interaction of the β -nitrogen with cupric ion is more stable than a five membered ring would be.⁹¹ Frazier and Bernhard⁸⁸ argued that the 1:1 complex is most questionable. They suggested that if the sulphonic acid groups are dissociated, then two protons cannot be produced by reaction with cupric ion. They suggested that a 2:1 complex is more plausible.

Sugars

Reducing sugars have been shown to reduce Amaranth at temperatures of 100, 77, 61 and 37.8°C to form a mixture of hydroamine species.⁹² The heating of aqueous fructose and glucose produces strongly reducing substances which are capable of reducing azo dyes. Banerjee *et al.*⁷⁷ suggested that the reducing action of lactose on dyes was due to glucose which composes half of the reducing molecule.

Singh⁹³ demonstrated that Amaranth decomposes when baked in cookies and that one of the decomposition compounds is 4-aminonaphthalene-1-sulphonic acid. The data presented indicated that the dye is reduced at the azo linkage, yielding 4-aminonaphthalene-1-sulphonic acid and 1-amino-2-naphthol-3,6-disulphonic acid (amino R-salt). However, neither amino R-salt nor the corresponding naphthoquinone could be isolated from baked products, possibly because they react with sucrose or dextrose. Baking soda

promoted decomposition of the dye and the decomposition increased markedly in the presence of dextrose. The 2-naphthol-3,6-disulphonic acid was assumed to oxidise readily to 1,2-naphthoquinone-3,6-disulphonic acid.

8.3.8 Methods of analysis

The analysis of synthetic food colours has been extensively reviewed within the scientific literature.^{48, 94–96} There are numerous methods published for the determination of synthetic food colours in food where early workers used paper and thin-layer chromatography but over the past 20 years high-performance liquid chromatography (HPLC),^{97–103} spectrophotometry,^{104–111} voltammetry^{112, 113} and capillary electrophoresis^{114–118} methods have been developed. The Association of Analytical Communities (AOAC) has also published numerous methods in relation to synthetic food dye analysis.¹¹⁹

Yoshioka and Ichihashi¹²⁰ published an HPLC-UV procedure for the determination of forty synthetic food colours in drinks and candies. The following food colours were analysed within 19 min using a short analytical column (50 mm × 4.6 mm i.d., 1.8 µm) at 50°C with gradient elution: Ponceau 6R, Tartrazine, Fast Yellow AB, Amaranth, Indigotine, Naphthol Yellow S, Chrysoine, Ponceau 4R, Sunset Yellow FCF, Red 10B, Orange G, Acid Violet 7, Brilliant Black PN, Allura Red AC, Yellow 2G, Red 2G, Uranine, Fast Red E, Green S, Ponceau 2R, Azorubine, Orange I, Quinoline yellow, Martius yellow, Ponceau SX, Ponceau 3R, Fast Green FCF, Eosine, Brilliant Blue FCF, Orange II, Orange RN, Acid Blue 1, Erythrosine, Amido Black 10B, Acid Red 52, Patent Blue V, Acid Green 9, Phloxine B, Benzyl Violet 4B, and Rose Bengal. The recoveries of these compounds added to soft drinks and candies at 5 µg/g ranged from 76.6 to 115.0%, and relative standard deviations (RSDs) were within 6.0%. The limits of detection and the limits of quantitation were 0.03 and 0.1 µg/g, respectively.

8.4 Illegal dyes

Spices are important ingredients used by the food manufacturing industry in the formulation of a wide range of processed foods. The colour and appearance of the bulk spice often dictates its economic price being interpreted as an indication of the freshness and quality of the product. Several incidents were reported within Europe in 2003–5 where imported spices and derivative foods were found to be adulterated with Sudan dyes or related colourants. During 2003, the EU-Rapid Alert System (RASFF) disseminated a series of notifications concerning the presence of Sudan dyes in chilli products and other foods such as spices, mixtures of spices, tomato sauces, pastas and sausages. Immediate action was taken on affected products such as

withdrawals/recalls and finally destruction according to Decision 2004/92/EC.¹²¹

Many illegal dyes are suspected to be genotoxic or carcinogenic, according to the EFSA^{122,123} and are illegal additives in foods within the European Community. Current agreements between the Member States of the European Community have stressed that food products containing greater than 0.5 mg/kg of any illegal dye are not fit for sale and should be withdrawn from the market.

Sudan I–IV, Sudan Red B, Sudan Red 7B, Sudan Orange G, Sudan Red G, Dimethyl Yellow, Orange II, Para Red and Toluidine dyes are all azo dyes and owing to their relatively high molecular mass and low polarity are oil soluble and notoriously difficult to analyse. Many methods have been developed for the determination of Sudan dyes and Para Red in foodstuffs and by HPLC or ultra-performance liquid chromatography (UPLC) with UV or diode array detector (DAD),^{124–129} MS^{130,131} and tandem MS (MS/MS)^{132–139} detection. Recently, UPLC UPLC/MS/MS was also used to analyse Sudan dyes and Para Red.¹⁴⁰ Lia *et al.*¹⁴¹ have published a UPLC-ESI-MS/MS method for the simultaneous determination of Sudan dyes (Sudan Red G, Sudan I, Sudan II, Sudan III, Sudan Red 7B and Sudan IV) and Para Red in food. Samples were extracted with acetonitrile, and water added into the extract. The supernatant was analysed by UPLC-MS/MS after refrigeration and centrifugation. The sample was separated on an Acquity BEH C18 column, and detected by MS/MS with the multiple reaction monitoring mode. Matrix calibration was used for quantitative testing of the method. The linear matrix calibrations of Sudan dyes and Para Red were 2–50 and 10–250 ng g⁻¹, respectively, and the regression coefficients were >0.9945. The recoveries were 83.4–112.3% with good coefficients of variation of 2.0–10.8%. The limits of detection were between 0.3 and 1.4 ng g⁻¹ for the six Sudan dyes, and between 3.7 and 6.0 ng g⁻¹ for Para Red. The limits of quantification were between 0.9 and 4.8 ng g⁻¹ for the six Sudan dyes, and between 12.2 and 19.8 ng g⁻¹ for Para Red.

Rebane *et al.*¹⁴² undertook a critical review of published determination methods of Sudan I–IV dyes. Liquid chromatography with UV (LC-UV) or visible detection and LC-MS were the dominating methods for analysis of Sudan I–IV dyes. Sudan dyes are usually found in food at mg/kg levels at which it may be necessary to use a pre-concentration step in order to attain the desired detection limits. Liquid–solid extraction is the dominating sample preparation procedure. In recent years it has been supplemented by ultrasonic-assisted extraction and pressurised liquid extraction. Various solid phase extraction types have been used for sample clean-up. The large majority of work uses conventional C18 columns and conventional LC eluents. Traditionally UV/visible detection has been the most frequently used.

Methods based on LC-MS/MS are particularly useful here because they can provide far lower detection limits compared to the equivalent LC-UV procedures and because by monitoring several characteristic ions simultaneously there is extra confirmation that a particular Sudan dye has been detected. Stuart¹⁴³ published a report exploring the feasibility of using a generic LC-MS/MS method based on standard addition for the quantitative determination of Sudans I–IV, Sudan Orange G, Sudan Red G, Sudan Red B, Sudan Red 7B, Para Red, Toluidine Red, Dimethyl Yellow, Orange II and Rhodamine B dyes in paprika powder. The dyes are extracted with a solvent of 100% acetonitrile at ambient temperature. Sample extracts are filtered, cleaned on C18 SPE cartridge and analysed by reverse-phase HPLC using an isocratic elution system using buffered water/acetonitrile and detection by MS. The method has been validated for the dyes at concentrations from 100 to 1000 µg/kg of paprika powder. Limits of detection were typically around 10 µg/kg for nine of the dyes, while recoveries were estimated to be in the range 80–110%. Precision is more variable and highly dependent on the nature of the dye and the level of spiking. Most of the nine have precision measured as a RSD between 3 and 13%, whereas for Sudan III, Sudan Red 7B and Toluidine Red the equivalent precision was in the range 3–40%. The dyes Rhodamine B, Orange II, Para Red and Sudan Orange G have poor performance data and could not be analysed in paprika spice by this method.

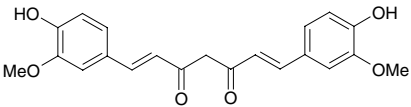
8.5 Natural dyes

8.5.1 Dicinnamoylmethane dyes

Curcumin (Turmeric, C.I. 75300, E100) is the only dicinnamoylmethane dye currently permitted for colouring food within the EU¹³ (Table 8.7).

Curcumin is obtained by solvent extraction of turmeric (i.e. the ground rhizomes of natural strains of *Curcuma longa* L.).¹³ The dried and ground roots of *Curcuma longa* L. are extracted with solvent and the solvent extract is concentrated under vacuum to produce a dark coloured oleoresin. In order to obtain a concentrated curcumin powder, the extract is purified by crystallisation. The product consists essentially of curcumin; i.e. the colouring principle (1,7-bis(4-hydroxy-3-methoxyphenyl) hepta-1,6-dien-3,5-dione) and its two desmethoxy derivatives in varying proportions. Minor amounts of oils and resins naturally occurring in turmeric may also be present. Curcumin is insoluble in water but soluble in alkalis, alcohol and glacial acetic acid. Curcumin stands up well to heat processing but is unstable to light and alkaline conditions where it degrades to vanillin and diferuloylmethane.

Table 8.7 Dicinnamoylmethane food colours permitted for use within the EU

Natural colour	Structure
<p>Curcumin (E100)</p> <p><i>Synonyms</i> – C.I. 75300, Turmeric</p> <p><i>Chemical names</i></p> <p>I 1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione</p> <p>$C_{21}H_{20}O_6$</p> <p>M.Wt 368.39</p> <p>II 1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione</p> <p>$C_{20}H_{18}O_5$</p> <p>M.Wt 338.39</p> <p>III 1,7-bis(4-hydroxyphenyl)hepta-1,6-diene-3,5-dione</p> <p>$C_{19}H_{16}O_4$</p> <p>M.Wt 308.39</p> <p><i>Acceptable daily intake</i></p> <p>SCF – No ADI</p> <p>JECFA – 5 mg/kg bodyweight/day¹⁴⁴</p> <p>EFSA – 3 mg/kg bodyweight/day¹⁴⁵</p>	

Methods of analysis for the determination of curcumin in food have been extensively reviewed by Scotter.³ The JECFA specification for curcumin prescribes a method based on spectrophotometric procedure.¹⁴⁶ Whilst HPLC is the most common technique used for the determination of curcumin, the separation and individual quantitation of the three curcuminoids is important because their extinction coefficients and stabilities vary.^{147–149} Additionally, when used in combination with annatto, the isomers of the yellow-coloured thermal degradation products of annatto exhibit similar chromatographic behaviour to the curcuminoids. Since the curcuminoids are not currently readily available as pure reference materials they normally require preparation from turmeric extracts, which is very time consuming.

8.5.2 Anthraquinone dyes

Carmines and carminic acid are obtained from aqueous, aqueous alcoholic or alcoholic extracts from Cochineal, which consists of the dried bodies of the female insect *Dactylopius coccus* Costa harvested from specific varieties of cacti in the Canary Islands, Chile and Peru.¹³ The colouring principle is carminic acid (Table 8.8).

Table 8.8 Anthraquinone food colours permitted for use within the EU

Natural colour	Structure
<p>Carmines (E120)</p> <p>Synonyms – C.I. 75740, cochineal, carminic acid.</p> <p>Chemical name – 7-β-D-glucopyranosyl-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxoanthracene-2-carboxylic acid (carminic acid); carmines is the hydrated aluminium chelate of this acid</p> <p>Empirical formula – $C_{22}H_{20}O_{13}$</p> <p>Molecular weight – 492.39</p>	

Aluminium lakes of carminic acid (carmines) can be formed in which aluminium and carminic acid are thought to be present in the molar ratio 1:2. In commercial products the colouring principle is present in association with ammonium, calcium, potassium or sodium cations, singly or in combination, and these cations may also be present in excess. Commercial products may also contain proteinaceous material derived from the source insect, and may also contain free carminate or a small residue of unbound aluminium cations. Carminic acid readily forms complexes with calcium and aluminium cations under high temperatures to produce a lake of carminic acid known as carmine.

Methods of analysis for the determination of carmine in food have been extensively reviewed by Scotter.³ Scotter reports that the most significant study by far for the development and validation of a quantitative method for the determination of carmine in foods is the collaborative study reported by Merino, Edberg and Tidriks.¹⁵⁰ Within the study, carminic acid was extracted by digesting samples in boiling HCl, cleaned up using RP-SPE and analysed using RP-HPLC with UV detection at 280 nm. The method was evaluated using internal quality control and collaboration between eleven laboratories. Samples of fruit jelly, liqueur, juice, yoghurt and ice cream were analysed and the limit of detection was 0.1 mg/L. External calibration was used and the calibration curve was linear up to 20 mg/L carminic acid. The mean recovery range for spiked samples was 85–94% with RSD_R values all below 12%. The authors concluded that the glucose link of carmine has a remarkable resistance to acid hydrolysis, hence reasonably strong acid could be used to break down sample matrices without significant analyte losses.

8.5.3 Carotenoid dyes

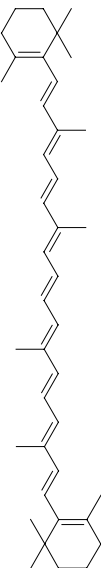
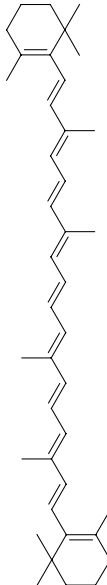
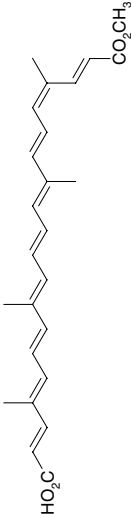
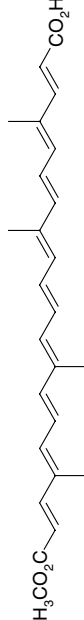
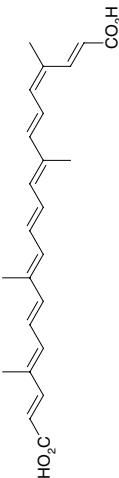

The carotenoids are one of the most important groups of natural pigments used as food dyes and comprise mainly hydrocarbon carotenes and oxygenated xanthophylls (Table 8.9).

Most of the carotenoid dyes suitable for food use are fat soluble and may be isolated using simple solvent extraction. Evaporation of the solvent yields a crude extract which may be purified further using recrystallisation.

Mixed carotenes are obtained by solvent extraction of natural strains of edible plants, carrots, vegetable oils, grass, alfalfa (lucerne) and nettle.¹³ The main colouring principle consists of carotenoids of which β -carotene accounts for the major part. α , γ -carotene and other pigments may be present. Besides the colour pigments, this substance may contain oils, fats and waxes naturally occurring in the source material. The most important source of plant carotenes is the fruit of the oil palm (*Elaeis guineensis*) which is a rich source of mixed carotenoids. Mixed carotenes may also be produced from natural strains of the algae *Dunaliella salina*, grown in large saline lakes located in Whyalla, South Australia. β -carotene is extracted using an essential oil resulting in a 20–30% suspension in edible oil. The ratio of *trans-cis* isomers is in the range of 50/50 to 71/29. The main colouring principle consists of carotenoids of which β -carotene accounts for the major part (60%), α -carotene (40%), lutein, zeaxanthin and β -cryptoxanthin may be present. Besides the colour pigments, this substance may contain oils, fats and waxes naturally occurring in the source material. The *cis*, *trans*, α , β -carotene mixture is considered more stable to oxidation than all-*trans* β -carotene.¹⁵¹ All carotenoid dyes are unstable to light and should be stored in the dark and under cool conditions; often an antioxidant such as ascorbyl palmitate or α -tocopherol is added to the dye.

β -carotene may be obtained by a fermentation process using a mixed culture of the two sexual mating types (+) and (–) of natural strains of the fungus *Blakeslea trispora*.¹³ The β -carotene is extracted from the biomass with ethyl acetate, or isobutyl acetate followed by isopropyl alcohol, and crystallised. The crystallised product consists mainly of *trans* β -carotene. Because of the natural process approximately 3% of the product often consists of mixed carotenoids, which is specific for the product.³ The shade of β -carotene is dependent on the concentration used and isomerisation. At low concentrations the shade is typically yellow-orange whereas at high concentrations it is orange-red. The all-*trans* form gives a redder colour than the basic orange. Emerton¹⁵¹ reports β -carotene to be insoluble in water and only slightly soluble in oil at ambient. β -carotene is reasonably light stable and only extremes in pH lead to pigment degradation. β -carotene is reasonably heat stable although as with all carotenoids it is susceptible to oxidation.

Table 8.9 Carotenoid food colours permitted for use within the EU

Natural colour	Structure
<p>Mixed carotenes (E160a (i))</p> <p>Synonyms – C.I. 75130, Food Orange 5</p> <p>Empirical formula – $C_{40}H_{56}$</p> <p>Molecular weight – 536.88</p>	
<p>β-carotene (E160a(ii))</p> <p>Synonyms – C.I. Food Orange 5</p> <p>Empirical formula – $C_{40}H_{56}$</p> <p>Molecular weight – 536.88</p>	
<p>Annatto (E160b)</p> <p>Synonyms – C.I. 75120, C.I. natural Orange 4</p> <p>Chemical name – A mixture of bixin and norbixin:</p>	
<p>Bixin</p> <p>6'-Methylhydrogen-9'-cis-6,6'-diapocarotene-6,6'-dioate</p> <p>6'-Methylhydrogen-9'-trans-6,6'-diapocarotene-6,6'-dioate</p>	
<p>Norbixin</p> <p>9'-Cis-6,6'-diapocarotene-6,6'-dioic acid</p> <p>9'-Trans-6,6'-diapocarotene-6,6'-dioic acid</p>	
<p>Empirical formulae</p> <p>Bixin $C_{25}H_{30}O_4$</p> <p>Norbixin $C_{24}H_{28}O_4$</p> <p>Molecular weights</p> <p>Bixin 394.51</p> <p>Norbixin 380.48</p>	

Paprika (E160c)

Synonyms – Paprika extract, paprika oleoresin

Chemical name – A mixture of capsanthin and capsorubin:

Capsanthin

(3R, 3'S, 5'R)-3,3'-dihydroxy- β ,k-carotene-6-one.

Capsorubin

(3S, 3'S, 5R, 5R')-3,3'-dihydroxy-k,k-carotene-6,6'-dione.

Empirical formulae

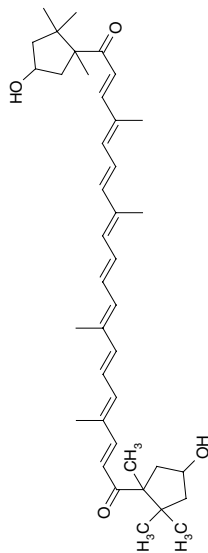
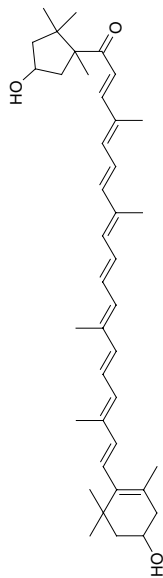
Capsanthin $C_{40}H_{56}O_3$

Capsorubin $C_{40}H_{56}O_4$

Molecular weights

Capsanthin 584.85

Capsorubin 600.85



Lycopene (E160d)

Synonyms – C.I. 75125, Natural Yellow ²⁷

Chemical name – ψ,ψ -carotene

Empirical formula – $C_{40}H_{56}$

Molecular weight – 536.85

Ethyl ester of β -Apo-8'-carotenoic acid (E160f)

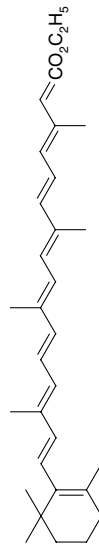
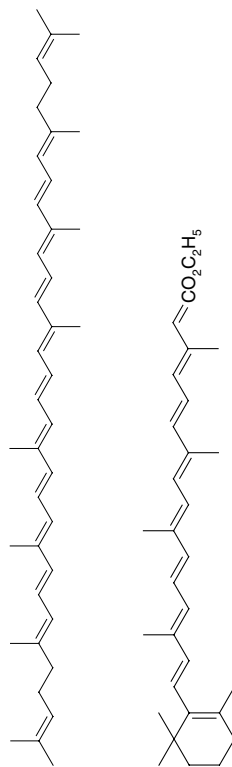
Synonyms – C.I. Food Orange 7, β -Apo-8'-Carotenoic Ester

Chemical name – β -apo-8'-carotenoic acid ethyl ester, ethyl

8'-apo- β -caroten-8'-oate

Empirical formula – $C_{32}H_{44}O_2$

Molecular weight – 460.70



(Continued)

Table 8.9 Continued

Natural colour	Structure
<p>Lutein (E161b)</p> <p>Synonym – Xanthophylls</p> <p>Chemical name – 3,3'-dihydroxy-d-carotene</p> <p>Empirical formula – $C_{40}H_{56}O_2$</p> <p>Molecular weight – 568.88</p>	
<p>Canthaxanthin (E161g)</p> <p>Synonym – C.I. Food Orange 8</p> <p>Chemical name – β-carotene-4,4'-dione</p> <p>Empirical formula – $C_{40}H_{52}O_2$</p> <p>Molecular weight – 564.86</p>	

Annatto extracts obtained from the seeds of the tropical shrub *Bixa orellana* L. (native to South America) are widely used for colouring many food commodities such as dairy products, flour confectionery, fish, soft drinks, meat products, snack foods and dry mixes.¹³ Annatto extracts are usually formulated to provide suitably stabilised forms in the colour range red-orange-yellow and are generally available as oil- or water-soluble solutions, suspensions, emulsions, encapsulated products or spray-dried powders. The principal colouring component of annatto seeds is the fat-soluble C₂₅ diapocaro-tenoid 9'-*cis*-bixin, which is the monomethyl ester of the water-soluble 9'-*cis*-norbixin. Annatto has traditionally been used for colouring bread-crumbs due to its ability to bind to protein in flour. However, the restrictions imposed by EU Directive¹¹ have reduced this usage. Dairy products are also often coloured with annatto. Cheese can be coloured with norbixin (e.g. Red Leicester).

Three main commercial processes are used to extract the pigment from dried annatto seeds. These are (i) direct extraction into oil, (ii) direct extraction into aqueous alkali or (iii) indirect extraction with solvents.¹⁵² Hot oil is used to facilitate isomerisation of the naturally occurring 9'-*cis*-bixin to the relatively more soluble *trans*-bixin. The major colouring principals produced by direct oil extraction are 9'-*cis*-bixin, all-*trans*-bixin and C17. This method is generally employed to provide a colour formulation suitable for fat- or oil-based products such as margarine. Direct aqueous alkali extraction produces alkali metal or ammonium salt solutions of 9'-*cis*-norbixin plus a small amount of the very poorly soluble all-*trans* isomer. In the indirect extraction of annatto, the pigments are extracted from the seeds with solvent, which is subsequently removed. This produces highly concentrated extracts consisting mainly of 9'-*cis*-bixin along with much lesser quantities of *trans*-bixin and 9'-*cis*-norbixin. The solvent-extracted pigment may be used as a dry powder, milled with vegetable oil to produce a suspension, or hydrolysed in aqueous alkali to produce a solution of norbixinate.

As with all other carotenoids, annatto extracts are susceptible to oxidative degradation. Colour loss also occurs upon prolonged exposure to light, elevated temperature, and in the presence of sulphur dioxide.¹⁵² The major thermal degradation products of annatto have been characterised as the yellow-coloured isomers and hydrolysis products of the *trans*-monomethyl ester of 4,8-dimethyltetradecahexaenedioic acid (C17).¹⁵³ The thermal degradation products of bixin and norbixin have been identified by Scotter.¹⁵³ Using HPLC with photodiode-array detection, ¹H NMR spectroscopy and MS Scotter showed that the main thermal degradation product of 9'-*cis*-bixin is *trans*-monomethyl ester of 4,8-dimethyltetradecahexaenedioic acid. This substance was shown to exist in different stereoisomeric configurations in solution and to be susceptible to hydrolysis, forming a range of substances analogous to bixin and norbixin. The results lead to a revised mechanism

for the thermal degradation of 9'-*cis*-bixin. Further work by Scotter *et al.*¹⁵⁴ studied the thermal stability of annatto food colouring in model systems and foods. HPLC with photodiode-array detection was used to monitor the isomerisation products of 9'-*cis*-bixin and its major coloured C17 degradation product. Headspace GC-MS was used to determine the degradation products toluene and *m*-xylene in the headspace of model systems and foods containing annatto heated *in situ*. Fish and cheese spiked with 9'-*cis*-norbixin produced *m*-xylene whereas control samples did not. Low levels (*ca.* 10–50 µg/kg) of *m*-xylene were detected in the headspace of annatto-coloured retail samples of custard powder, extruded snacks, margarine and breadcrumbs. Higher levels of *m*-xylene were detected in the headspace of kippers (*ca.* 150–200 µg/kg) and observed in the headspace of Red Leicester type cheese (not quantified). The findings indicated that annatto is readily degraded to form both coloured degradation products and the aromatics *m*-xylene and, to a lesser extent, toluene. In practice however, degradation is slow under heating conditions normal for foods. Neither aromatic species was detected in the headspace of any food studied above 200 µg/kg.

Mercandte *et al.*¹⁵⁵ isolated five apocarotenoids in trace amounts from the seed coat of the *Bixa orellana* L. fruits. Their structures were established by means of UV-visible, 400 and 500 MHz ¹H and 100 and 120 MHz ¹³C NMR spectroscopy, and MS. Methyl (7Z,9Z,9'Z)-apo-6'-lycopenoate, methyl (9Z)-apo-8'-lycopenoate, methyl (all-E)-apo-8'-lycopenoate are new carotenoids, and the other two, methyl (all-E)-8'-apo-β-caroten-8'-oate and methyl (all-E)-apo-6'-lycopenoate, have not been previously found in annatto.

Paprika extract is obtained by solvent extraction of the natural strains of paprika, which consists of the ground fruits pods, with or without seeds, of *Capsicum annum* L., and contains the major colouring principals of this spice. The major colouring principals are capsanthin and capsorubin as well as their dilaurate esters. A wide variety of other coloured compounds is known to be present. Only the following solvents may be used in the extraction: methanol, ethanol, acetone, hexane, dichloromethane, ethyl acetate and carbon dioxide. Emerton¹⁵¹ reports paprika extracts to be reasonably stable to heat and light but may degrade on prolonged exposure to sunlight. Water-miscible emulsions are reported stable to changes in pH.

Lycopene is obtained by solvent extraction of the natural strains of red tomatoes (*Lycopersicon esculentum* L.) with subsequent removal of the solvent.¹³ The major colouring principal of tomatoes is lycopene, minor amounts of other carotenoid pigments may be present. Beside the other colour pigments the product may contain oils, fats, waxes and flavour components naturally occurring in tomatoes. Lycopene is the major pigment of tomato (up to 90%) and exists mainly in the *trans* form.³ It is highly conjugated (i.e. 13 double bonds) which accounts for its high colour intensity.

Lutein is obtained by solvent extraction of the natural strains of edible fruits and plants, grass, lucerne (alfalfa) and *tagetes erecta*.¹³ The main colouring principal consists of carotenoids of which lutein and its fatty acid esters account for the major part. Variable amounts of carotenes will also be present. Lutein may contain fats, oils and waxes naturally occurring in the plant material. A typical lutein extract contains approximately 10% lutein (mainly in the ester form) although following refining concentrations of over 30% can be achieved.¹⁵¹

Canthaxanthin (β -carotene-4,4'-dione) occurs in nature within fish flesh and is the dye mainly responsible for the pink colour of flamingo feathers.¹⁵⁶ The only commercial source is produced by chemical synthesis so this dye is classified as being 'nature identical'. Commercially produced canthaxanthin is predominantly in the all-*trans* form.¹⁵¹ Within the EU the use of canthaxanthin for colouring food is severely restricted¹³ and is currently only permitted (up to 15 mg/kg) for colouring 'Saucisses de Strasbourg' where it produces a red colour.

β -Apo-8'-carotenoic acid ethyl ester is the acid form of the aldehyde carotenoid β -apo-8'-carotenal and is produced by chemical synthesis to yield a predominantly all-*trans* form. In this form it is known as a 'nature identical' dye and is synthesised to a purity of <98%. As with all carotenoids, the all-*trans* isomer readily isomerises to yield a mixture of *cis* and *trans* isomers especially when heated to >60°C and/or exposed to UV light.¹⁵¹

The methods of analysis for the determination of carotenoid dyes in food have been extensively reviewed by Scotter.³ Scotter reported that owing to the unstable nature of carotenoids, especially during isolation, to light, heat and oxygen, special precautions are necessary during analysis. The isoprenoid structure of carotenoids is manifested in a series of conjugated diene bonds that confer useful spectral properties, therefore carotenoids exhibit characteristic absorption spectra in the UV-VIS range that have diagnostic features (such as *cis-trans* isomerism), which are useful for analytical detection and measurement. Within Scotter's excellent review³ he reports there to be no standard extraction procedures for carotenoids due to the wide variety of food products and animal samples containing them, and the range of different carotenoids that may be found. Scotter³ highlights that one of the main issues surrounding the analysis of carotenoids is the diversity, geometric isomerism and availability of standard materials. Their inherent instability requires storage under inert conditions (typically under an atmosphere of argon or nitrogen at -80°C) with regular purity checking using HPLC. Whilst most of the main carotenoids are available commercially as analytical standards, they are costly. For quantitative analysis, β -apo-8'-carotenal or echinenone are occasionally used as internal standards. Scotter³ reported that most of the published analytical methods relate to their determination in source materials or for nutritional purposes, rather

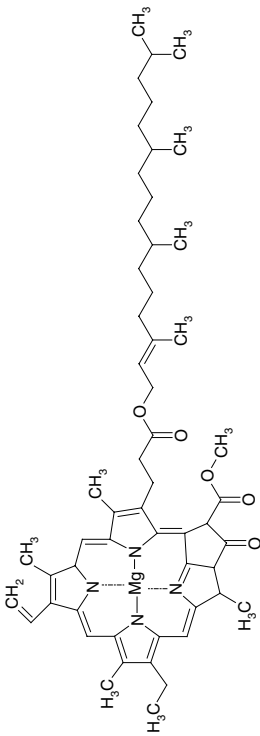
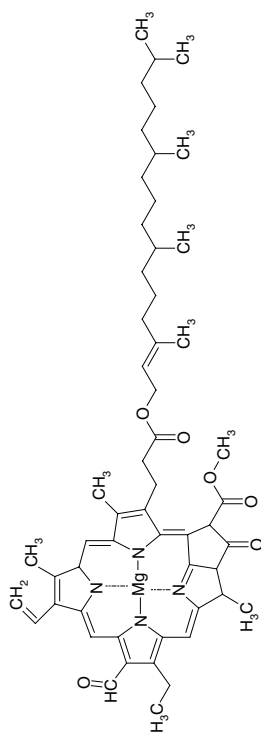
than as added colourings but several allow the determination of multiple analytes. Solvent extraction is generally used with some form of selective clean-up such as partition and/or SPE followed by reverse-phase HPLC.^{157–160} Several authors have reviewed extraction methods for carotenoids in foodstuffs.^{3,161–164} Depending upon the fat content of the sample, saponification or enzymatic hydrolysis is required. Saponification (alkaline hydrolysis) has been widely used to enhance carotenoid isolation where it is particularly effective for removing colourless contaminating lipid material and for destroying chlorophyll. Saponification also helps to solubilise large quantities of other food components such as proteins and carbohydrates which would otherwise interfere with the extraction and analysis. It should be noted that saponification will hydrolyse carotenoid esters and it is therefore to be avoided when attempting to determine esterified carotenes such as ethyl ester of β -apo-8'-carotenoic acid unless the objective is to measure the free acid. It is important that the formation of artefacts is minimised during extraction, saponification and work-up, e.g. multiple *cis*- isomers and oxidation products. Rodríguez-Bernaldo de Quirós and Costa¹⁶⁵ have summarised different saponification conditions in various samples and recommended that as a general rule, samples with low fat content should be saponified under mild conditions and high-fat samples under stronger conditions. Reversed-phase HPLC with PDA detection is used for quantitation and to spectrally characterise the pigments. Most methods demonstrate sufficient sensitivity but only relatively few methods have been fully validated through collaborative trial. Several methods are available for the determination of canthaxanthin, β -apo-8'-carotenal and the ethyl ester of β -apo-8'-carotenoic acid in animal feeds^{166,167} which follow similar extraction and measurement protocols.

8.5.4 Porphyrin dyes

Chlorophylls are obtained by solvent extraction of natural strains of edible plant material, grass, lucerne and nettles.¹³ Commercially, chlorophylls are derived from purified extracts of alfalfa grass, lucerne, nettles and grasses.¹⁶⁸ During the subsequent removal of solvent, the naturally present coordinated magnesium may be wholly or partly removed from the chlorophylls to give the corresponding pheophytins. The principal colouring matters are the pheophytins and magnesium chlorophylls. The extracted product, from which the solvent has been removed, contains other pigments such as carotenoids as well as oils, fats and waxes derived from the source material. As a result of its inherent instability^{169,170} chlorophyll itself is limited in its use as a food colour (Table 8.10).

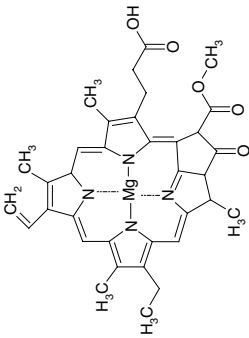
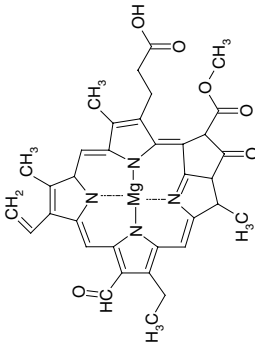
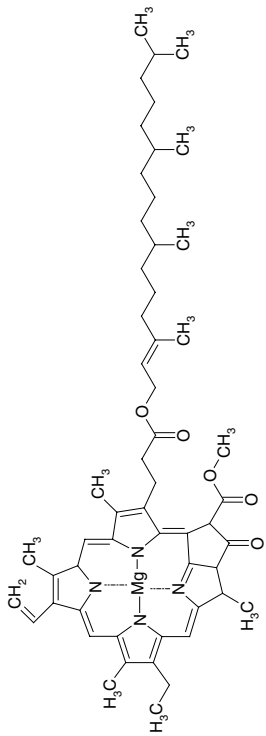
Scotter and Castle⁷⁴ report that chlorophyll destruction can proceed as an acid-, base- or enzyme-catalysed reaction. Weak acids liberate the Mg

Table 8.10 Porphyrin food colours permitted for use within the EU

Natural colour	Structure
<p>Chlorophyll (E140i)</p> <p>Synonyms – C.I. Natural Green 3, Magnesium Chlorophyll, Magnesium Pheophytin</p> <p>Chemical names – The principal colouring matters are the pheophytins and magnesium chlorophylls. The major colouring principals are:</p> <p>Phytol (132R,17S,18S)-3-(8-ethyl-132-methoxycarbonyl-2,7,12,18-tetramethyl-13'-oxo-3-vinyl-131-132-17,18-tetrahydrocyclopenta [at]-porphyrin-17-yl)propionate, (Pheophytin a), or as the magnesium complex (Chlorophyll a), and</p> <p>Phyl (132R,17S,18S)-3-(8-ethyl-7-formyl-132-methoxycarbonyl-2,12,18-trimethyl-13'-oxo-3-vinyl-131-132-17,18-tetrahydrocyclopenta[at]-porphyrin-17-yl)propionate, (Pheophytin b), or as the magnesium complex (Chlorophyll b)</p> <p>Empirical formulae</p> <p>Chlorophyll a (magnesium complex): $C_{55}H_{72}MgN_4O_5$</p> <p>Chlorophyll a: $C_{55}H_{74}N_4O_5$</p> <p>Chlorophyll b (magnesium complex): $C_{55}H_{70}MgN_4O_6$</p> <p>Chlorophyll b: $C_{55}H_{72}N_4O_6$</p> <p>Molecular weights</p> <p>Chlorophyll a (magnesium complex): 893.51</p> <p>Chlorophyll a: 871.22</p> <p>Chlorophyll b (magnesium complex): 907.49</p> <p>Chlorophyll b: 885.20</p>	 

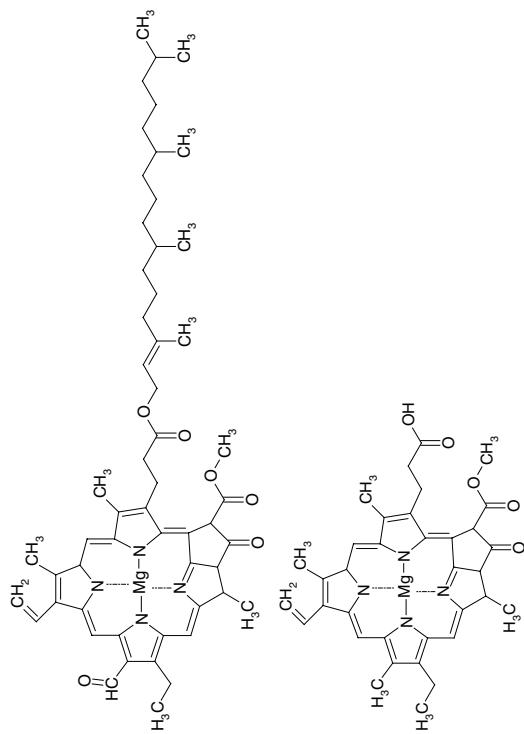
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Table 8.10 Continued

Natural colour	Structure
<p>Chlorophyllins (E140ii)</p> <p>Synonyms – C.I. Natural Green 5, Sodium Chlorophyllin, Potassium Chlorophyllin</p> <p>Chemical names – The major colouring principals in their acid forms are:</p> <p>– 3-(10-carboxylato-4-ethyl-1,3,5,8-tetramethyl-9-oxo-2-vinylphorbin-7-yl)propionate (chlorophyllin a)</p> <p>and</p> <p>– 3-(10-carboxylato-4-ethyl-3-formyl-1,5,8-trimethyl-9-oxo-2-vinylphorbin-7-yl)propionate (chlorophyllin b)</p> <p>Depending on the degree of hydrolysis the cyclopentenyl ring may be cleaved with the resultant production of a third carboxyl function.</p> <p>Empirical formulae</p> <p>Chlorophyllin a (acid form): $C_{34}H_{34}N_4O_5$</p> <p>Chlorophyllin b (acid form): $C_{34}H_{32}N_4O_6$</p> <p>Molecular weights</p> <p>Chlorophyllin a: 578.68</p> <p>Chlorophyllin b: 592.66</p>	  
<p>Copper complexes of chlorophylls (E141i)</p> <p>Synonyms – C.I. Natural Green 3, Copper Chlorophyll, Copper Pheophytin</p> <p>Chemical names – The principal colouring matters are the copper pheophytins:</p> <p>13'-oxo-3-vinyl-131-132-17,18-tetrahydrocyclopenta[1]-porphyrin-17-yl]propionate] copper (III) (Copper Chlorophyll a)</p> <p>[Phytyl (132R,17S,18S)-3-(8-ethyl-7-formyl-132-methoxycarbonyl-2,12,18-trimethyl-13'-oxo-3-vinyl-131-132-17,18-tetrahydrocyclopenta[1]-porphyrin-17-yl)propionate] copper (II) (Copper Chlorophyll b)</p>	

Copper chlorophyll a: $C_{55}H_{72}CuN_4O_5$
Copper chlorophyll b: $C_{55}H_{70}CuN_4O_6$

Copper chlorophyll a: 932.75
Copper chlorophyll b: 946.73



Copper complexes of chlorophyllins (E141ii)
Synonyms – Sodium Copper Chlorophyllin, Potassium Copper

Green 5

Chemical names – The major colouring principals in their acid forms are:

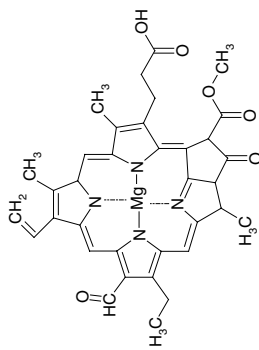
3-(10-Carboxylato-4-ethyl-1,3,5,8-tetramethyl-9-oxo-2-

vinylphorbin-7-yl)propionate, copper complex (Copper chlorophyllin a), and

3-(10-Carboxylato-4-ethyl-3-formyl-1,5,8-trimethyl-9-oxo-2-vinylphorbin-7-yl) propionate, copper complex (Copper chlorophyllin b)

Copper chlorophyllin a (acid form): $C_{34}H_{32}CuN_4O_5$
Copper chlorophyllin b (acid form): $C_{34}H_{30}CuN_4O_6$

Copper chlorophyllin a: 640.20
Copper chlorophyllin b: 654.18



atom bound to the porphyrin ring to form pheophytins by substitution with hydrogen. This results in a colour change from green to dull brown. Lin *et al.*¹⁷¹, report that the major organic acids involved in the degradation of chlorophylls are acetic acid and 5-oxopyrrolidinecarboxylic acid. The alkali salts of chlorophyllins are obtained by the saponification of a solvent extract of natural strains of edible plant material, grass, lucerne and nettles. The saponification removes the methyl and phytol ester groups and may partially cleave the cyclopentenyl ring. The acid groups are neutralised to form the salts of potassium and/or sodium.

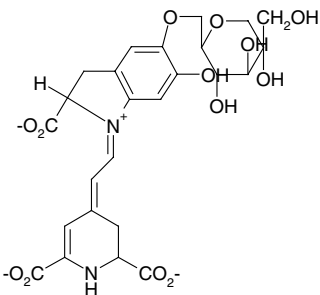
Copper chlorophylls are obtained by addition of copper ions to the saponified extract of edible plant material (e.g. grass, lucerne and nettles). The saponification step removes the methyl and phytol ester groups to yield chlorophyllin. Saponification may also partially cleave the cyclopentenyl ring. The product, from which the solvent has been removed, contains other pigments such as carotenoids as well as fats and waxes derived from the source material. The replacement of the central magnesium ion with copper produces a more stable complex with high tinctorial power.¹⁷²

The methods of analysis for the determination of chlorophylls and copper complexes of chlorophyllins in food have been extensively reviewed by Scotter³ and Wood *et al.*⁹⁶

8.5.5 Betalaine dyes

Beet red (Table 8.11) is obtained from the roots of natural strains of red beets (*Beta vulgaris* L. var. rubra) by pressing crushed beet as press juice or by aqueous extraction of shredded beet roots and subsequent enrichment in the active principal.¹³

Table 8.11 Betalaine food colours permitted for use within the EU

Natural colour	Structure
<p>Beetroot Red (E162)</p> <p>Synonyms – Betanin</p> <p>Chemical name – (S-(R',R')-4-(2-(2-Carboxy-5- (β-D-glucopyranosyloxy)-2,3-dihydro-6-hydroxy-1H-indol-1-yl)ethenyl)-2,3-dihydro-2,6-pyridine-dicarboxylic acid; 1-(2-(2,6-dicarboxy-1,2,3,4-tetrahydro-4-pyridylidene)ethylidene)-5-β-D-glucopyranosyloxy)-6-hydroxyindolium-2-carboxylate</p> <p>Empirical formulae – $C_{24}H_{26}N_2O_{13}$</p> <p>Molecular weights – 550.48</p>	

The colour is composed of different pigments all belonging to the class betalaine. The main colouring principal consists of betacyanins (red) of which betanin accounts for 75–95%. Minor amounts of betaxanthin (mainly vulgaxanthin) and degradation products of betalaines (light brown) may be present. Besides the colour pigments the juice or extract consists of sugars, salts and/or proteins naturally occurring in red beets. The solution may be concentrated and some products may be refined in order to remove most of the sugars, salts and proteins. Azeredo¹⁷³ reported that both betacyanins and betaxanthins are water soluble, are insoluble in organic solvents and are susceptible to degradation due to heat, light, oxygen and pH change.

The methods of analysis for Beetroot Red in food have been extensively reviewed by Scotter.³ Scotter comments that over the past 50 years, there has been considerable interest in the pigment composition of red beets and other *Centrospermae*, including many studies on extraction, colourant content and stability of more than 50 betalain colour principals from a wide variety of plant sources. This is reflected in the large number of scientific articles available; however, apart from studies focusing on beet extracts and subsequent colour formulations, very few articles could be found describing methods of extraction and analysis of added beet colour in foods and beverages. Commission Directive 2008/128¹³ prescribes the identification and the minimum content of the colouring material (measured by spectrophotometry). The JECFA specification¹⁷⁴ prescribes an assay procedure based on spectrophotometric measurement at 530 nm and pH 5.0.

Reversed-phase HPLC is now the method of choice for the separation, identification and quantitation of beet pigments and there are many literature references available.^{175–179}

8.5.6 Anthocyanin dyes

Anthocyanins are obtained by extraction with sulphited water, acidified water, carbon dioxide, methanol or ethanol from the natural strains of vegetables and edible fruits.¹³ Anthocyanins contain common components of the source material, namely anthocyanine, organic acids, tannins, sugars, minerals, etc., but not necessarily in the same proportions as found in the source material. As with other polyphenolic substances, anthocyanins occur naturally as glycosides of polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium (or flavylum) salts, i.e. the aglycones anthocyanidins (Table 8.12).

Anderson and Jordheim¹⁸⁰ stated that more than 500 individual anthocyanins have been identified where of the known naturally occurring aglycones, six occur most frequently in plants; namely, pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin. The sugars most commonly

Table 8.12 Anthocyanin food colours permitted for use within the EU

Natural Colour	Structure
Anthocyanins (E163) <i>Chemical names</i> 3,3',4',5',7-Pentahydroxy-flavylium chloride (cyanidin) 3,4',5,7-Tetrahydroxy-3'-methoxyflavylium chloride (peonidin) 3,4',5,7-Tetrahydroxy-3',5'-dimethoxyflavylium chloride (malvidin) 3,5,7-Trihydroxy-2-(3,4,5-trihydroxyphenyl)-1-benzopyrylium chloride (delphinidin) 3,3',4',5,7-Pentahydroxy-5'-methoxyflavylium chloride (petunidin) 3,5,7-Trihydroxy-2-(4-hydroxyphenyl)-1-benzopyrylium chloride (pelargonidin)	
<i>Empirical formulae</i> Cyanidin: C ₁₅ H ₁₁ O ₆ Cl Peonidin: C ₁₆ H ₁₃ O ₆ Cl Malvidin: C ₁₇ H ₁₅ O ₇ Cl Delphinidin: C ₁₅ H ₁₁ O ₇ Cl Petunidin: C ₁₆ H ₁₃ O ₇ Cl Pelargonidin: C ₁₅ H ₁₁ O ₆ Cl <i>Molecular weights</i> Cyanidin: 322.6 Peonidin: 336.7 Malvidin: 366.7 Delphinidin: 340.6 Petunidin: 352.7 Pelargonidin: 306.7	

bonded to these are glucose, galactose, rhamnose and arabinose. The colour shade obtained when using an anthocyanin extract is highly dependent on the source material and pH. Mazza *et al.*¹⁸¹ report that in acidic solutions, four anthocyanin species exist in equilibrium: the quinoidal base, the flavylium cation, the pseudo base and the chalcone. Anthocyanins are generally light and heat stable but pH is the most important factor affecting anthocyanin visual appearance.¹⁸²

The methods of analysis for anthocyanins in food have been extensively reviewed by Scotter.³ Commission Directive 2008/128/EC¹³ defines the method of assay in the specifications is based on spectrophotometric measurement at pH 3.0 between 515 and 535 nm, with reference to a prescribed extinction coefficient in 0.01% HCl. There are a large number of published articles on analytical methods for anthocyanins, as well as several detailed reviews.^{161,162,183–189} However, as with Beetroot Red, these have been primarily concerned with optimisation of extraction, separation of individual anthocyanins, qualitative characterisation, identification and structural elucidation rather than with the determination of anthocyanin colours added to foodstuffs.

8.5.7 Melanoidin dyes (caramels)

Caramel is the name given to the amorphous dark brown colouring material formed by heating food grade carbohydrates in the presence of selected accelerators. Four distinct classes of caramel can be distinguished.¹³

- Class I (Plain Caramel, Caustic Caramel, E150a) – Prepared by the controlled heat treatment of carbohydrates (commercially available food grade nutritive sweeteners which are the monomers glucose and fructose and/or polymers thereof, e.g. glucose syrups, sucrose, and/or invert syrups, and dextrose). To promote caramelisation, acids, alkalis and salts may be employed, with the exception of ammonium compounds and sulphites.
- Class II (Caustic Sulphite Caramel, E150b) – Prepared by the controlled heat treatment of carbohydrates (commercially available food grade nutritive sweeteners which are the monomers glucose and fructose and/or polymers thereof, e.g. glucose syrups, sucrose, and/or invert syrups, and dextrose) with or without acids or alkalis, in the presence of sulphite compounds (sulphurous acid, potassium sulphite, potassium bisulphite, sodium sulphite and sodium bisulphite); no ammonium compounds are used.
- Class III (Ammonia Caramel, E150c) – Prepared by the controlled heat treatment of carbohydrates (commercially available food grade nutritive sweeteners which are the monomers glucose and fructose and/or polymers

thereof, e.g. glucose syrups, sucrose, and/or invert syrups and dextrose) with or without acids or alkalis, in the presence of ammonium compounds (ammonium hydroxide, ammonium carbonate, ammonium hydrogen carbonate and ammonium phosphate); no sulphite compounds are used.

- Class IV (Sulphite Ammonia Caramel, E150d) – Prepared by the controlled heat treatment of carbohydrates (commercially available food grade nutritive sweeteners which are the monomers glucose and fructose and/or polymers thereof, e.g. glucose syrups, sucrose, and/or invert syrups and dextrose) with or without acids or alkalis in the presence of both sulphite and ammonium compounds (sulphurous acid, potassium sulphite, potassium bisulphite, sodium sulphite, sodium bisulphite, ammonium hydroxide, ammonium carbonate, ammonium hydrogen carbonate, ammonium phosphate, ammonium sulphate, ammonium sulphite and ammonium hydrogen sulphite).

In the UK, caramels account for approximately 90% by weight of the total colouring agents added to food.³ Of the four classes available, Classes I and IV are used for beverages (whiskies and soft drinks respectively), use of Class II in the UK is negligible, and Class III is used in a wide range of non-beverage foods and in beers.

The methods of analysis for caramel dyes in food have been extensively reviewed by Scotter³ and Wood *et al.*⁹⁶ Commission Directive 2008/128/EC¹³ prescribes separate definitions and purity criteria for E150a, E150b, E150c and E150d. A general specification for caramel colours is prescribed by JECFA containing detailed specifications for each class of caramel.¹⁹⁰ Both specifications prescribe a series of identification tests for classification/colour binding based on spectrophotometry along with various purity tests, which in the JECFA specification include total nitrogen and total sulphur content. Burch *et al.*¹⁹¹ have reviewed the extraction of caramels from complex food matrices. Over the past 20 years numerous methods using HPLC and more recently capillary electrophoresis have been developed for the determination of caramels in food.^{192–202}

8.6 Conclusions

Within this chapter a general review has been given of major substances currently used to colour food within the UK and the EU. The number and chemical diversity of substances used to colour food is large and it seems as though we now have a substance to colour practically any food. However, the list of permitted substances used to colour food is highly likely to decrease, rather than increase, in the future. There is growing evidence to justify a reduced use of food colour additives and also the possible ban of certain synthetic food colours within Europe as a whole. The UK FSA is publishing

lists of product ranges from food manufacturers, retailers and caterers that do not contain the six food colours associated with possible hyperactivity in young children. The Agency is publicising the product ranges to encourage the food industry to participate in the voluntary ban. The voluntary ban was agreed by UK ministers in 2010.

Extensive research is still being undertaken on the analysis of both legal and illegal dyes in food and methods of analysis tend to be heading more towards the use of LC-MS/MS rather than the classic spectrophotometric methods used 20–30 years ago.

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